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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

THERMODYNAMIC PROPERTIES OF LIQUID WATER TO 80° AND 12000 KGM.

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TABLE OF CONTENTS.

PAGE.
Introduction 310
Method 312
  Previous Use of the Method 312
  Description of the Apparatus 314
  Correction for the Distortion of the Vessel 316
  Experimental Procedure 319
    In Determining Compressibility 319
      Calibration of Manganin Coil 320
      Formulas 325
    In Determining Dilatation 326
The Data 328
  Compressibility at Low Pressures 328
  Dilatation at Low Pressures 330
  Compressibility at High Pressures 331
  Dilatation at High Pressures 334
Discussion of the Results 336
  Table of Volumes 338
    Method of Construction 336
  Various Thermodynamic Quantites 337
    Compressibility, $\left(\frac{\partial v}{\partial p}\right)_\tau$ 340
    Dilatation, $\left(\frac{\partial v}{\partial \tau}\right)_p$ 344
    Work of Compression, $W = -\int p \left(\frac{\partial v}{\partial p}\right)_\tau dp$ 346
    Heat of Compression, $Q = -\tau\int\left(\frac{\partial v}{\partial \tau}\right)_p dp$. 347
    Change of Internal Energy, $\Delta E = W + Q$ 348
    Pressure Coefficient, $\left(\frac{\partial p}{\partial \tau}\right)_v$ 349
    Specific Heat at Constant Pressure, C_p 351
    Specific Heat at Constant Volume, C_v 352
    Thermal Effect of Compression, $\left(\frac{\partial \tau}{\partial p}\right)_\varphi$ 354
    Adiabatic Compressibility, $\left(\frac{\partial v}{\partial p}\right)_\varphi$ 355
Volume of Kerosene as a Function of Temperature and Pressure . . 356
Compressibility and Dilatation of Ice VI 359

INTRODUCTION.

THIS paper is in the nature of a supplement to a former paper on the properties of water in the liquid and the solid forms.[1] The solid forms were studied over a range of 20,000 kgm./cm.^{2}, and from $-80°$ to $+76°$, but the study of the liquid reached only from the lowest temperature of its existence to about $+20°$. Above 0°, measurements were made on the liquid at only 20°. The two measurements, at 0° and 20° were sufficient to give the mean dilatation between 0° and 20°, but not the variation of dilatation with temperature. It was assumed in the earlier paper that the variation of dilatation with temperature became negligible at high pressures, since this seemed to be the most plausible assumption in view of all the data then available.

In this present paper the study of the liquid has been continued from 20° to 80°, and to 12000 kgm. The pressure range is greater than that of the preceding paper by about 2,500 kgm. The range is not great enough to entirely cover the region of stability of the liquid, but it is as great as it was convenient to cover with the method used here, which is different from that of the former work. It has the advantage of very much greater rapidity of operation, but since it depends on the complete elastic integrity of the steel pressure cylinders it is not possible to reach so high pressures with it as with the former method. [The former limit of 9500 kgm. was set by the freezing of the liquid and was not due to any limitation of the method.] Nevertheless, it may be hoped that the present temperature and pressure ranges are both wide enough to give a fairly complete idea of the nature of the effects to be expected at high pressures with varying temperature.

Measurements of the dilatation have been made at four temperatures, so that it has been possible to find the variation of dilatation with temperature at any pressure. Perhaps the most unlooked for feature disclosed by the measurements is the fact, contrary to the assumption of the first paper, that the variation of dilatation with temperature does not become vanishingly small at high pressures, but reverses in sign. This means that while at low pressures the volume increases more and more rapidly with rising temperature, at high pressures the expansion becomes more slow at high temperatures.

The data of this paper are sufficient to completely map out the *p-v-t* surface over the domain in question: Both the first and second derivatives are therefore completely determined, so that we now have all the data at hand for the determination of any one of the thermodynamic properties of the liquid. This means that we are in a position to find such quantities as the specific heats, change of internal energy, adiabatic temperature rise etc., as well as the more easily determined compressibility and thermal dilatation. The latter part of the paper, after the discussion of the method and the presentation of the data in the first part, is occupied with the computation of these various thermodynamic quantities. The accuracy of some of these is probably not very great, because the error in the second derivative of an experimental quantity may be considerable. It has, therefore, seemed best to give the general view of the nature of the quantities which is offered by a graphical representation, rather than to give tables, with the tacit assumption of greater accuracy which usually goes with a set of tables. In spite of the lower order of accuracy of some of these thermodynamic quantities, it has still seemed well worth while to give them, since even the general trend of some of the quantities, such as the specific heats, has not been hitherto known with relation to pressure.

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[1] Bridgman, These Proceedings, **47,** 439–558 (1912).

The data presented here are only the beginning of a projected study of the characteristic surface under high pressures for a number of liquids. The measurements have already been carried through for twelve other liquids beside water. The purpose of this study is ultimately the development of a theory of liquids, since it would seem that a much more intimate grasp of the nature of the forces at work in a liquid would be afforded by a study over a wide pressure range, than over the comparatively low pressures hitherto used. It must be admitted, however, that this broader purpose is not particularly furthered by this work on water, because of the well known abnormalities of this substance. In the previous paper several abnormalities had been shown to exist at low pressures. In this paper, new abnormalities are found at higher pressures. Water gives the appearance of becoming completely normal only at the higher temperatures and pressures of the range used here, but of course whether this is really normal or not cannot be told until the behavior of normal liquids has been discovered. The full significance of the present data, in their bearing on such questions as the polymerization of the liquid, for example, cannot appear until after the discovery of the laws for entirely normal liquids. The investigation of water before that of normal liquids was undertaken for two reasons; firstly because of the desire to complete the work for water already begun, and secondly because in this and the following investigation a new method for determining the compressibility was to be used, which had not yet been proved to be reliable, but which could be tested by a comparison of the results obtained by this method with those already obtained by another method at lower temperatures for water.

In addition to the data for liquid water, two other quantities were determined incidentally in the course of the work, and are given at the end of the paper. One of these is the experimental measurement of the compressibility and thermal dilatation of ice VI between 0° and 20° and 6360 and 10,000 kgm. The other is the measurement of the volume of kerosene up to 12,000 kgm. and between 20° and 80°.

The Method.

The method in its fundamental idea is as simple as it would well be possible to devise. The substance, whose compressibility or thermal dilatation is to be measured, is placed in a heavy steel cylinder in which pressure is produced by the advance of a piston of known cross section. The change of volume, given by the distance of advance of the piston, is measured as a function of the pressure. The method is simple, rapid, and above all, applicable to the highest pressures. But there are a number of corrections which must be made, often difficult to determine, which doubtless account for the slight use which has been made hitherto of the method. Apparently, with the exception of the present work, it has been used recently only by Tammann,[2] and by Parsons and Cook.[3] Tammann and Parsons and Cook applied it only to the measurement of compressibility, reaching pressures of about 4000 kgm. The author has previously applied it to the measurement of the thermal dilatation of water at temperatures below 0° C. over a pressure range of about 6500 kgm.

The most serious of the errors which readily occur to one is that of leak. It is almost essential to the success of the method to secure a piston absolutely free from leak, and this has hitherto been a matter of some difficulty at high pressures. Tammann did not entirely secure this freedom from leak, but avoided it in large measure by the use of a very heavy oil, such as castor oil, and still further lessened the error by correcting for the slight amount of leak by measuring the amount of liquid which escaped past the piston in a given time. This method would not be applicable to the highest pressures, however, because of the freezing of the oil. Parsons and Cook were able to secure entire freedom from leak up to 4000 kgm. by the employment of a cupped leather washer combined with a brass disc of special design. It has been the experience of all those who have worked with high pressures, however, that no leather washer is capable of standing pressures very much in excess of the limit of 4500 kgm., since the leather rapidly disintegrates under the pressure. In the present work the same form of packing was used which was used in the previous work on the freezing of water and mercury under pressure. This has been proved in the previous paper to be absolutely free from leak up to the highest pressures which can be sustained by the steel containing vessels. In the present work this same packing has proved itself to be reliable for the purposes of this method.

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[2] A. D. Cowper and G. Tammann, ZS. Phys. Chem., **68**, 281–288 (1909).
[3] Parsons and Cook, Proc. Roy. Soc. A, **85**, 332–349 (1911).

The question of the method of measuring pressure is also of considerable importance in using this method, since the usual measuring devices, such as a Bourdon gauge, cannot be applied, for reasons to be discussed later, and attempts to calculate the pressure directly from the force required to produce motion of the piston are likely to be in error because of the friction of the packing. Parsons and Cook did, however, adopt this latter method, and computed the pressure from the known force required to move the piston. The effect of the friction of the packings was allowed for in as large a degree as possible by taking the mean of the readings during increasing and decreasing pressure, assuming that the friction remained constant. The results obtained by Parsons and Cook in this way were surprisingly good. That the friction did remain fairly constant was indicated by the constancy of the results and the fact that the curve nearly always returned to the starting point; but it is doubtful if the method would work at very much higher pressures because of the increase of friction due to the flow of the softer parts of the piston. The brass washers used by Parsons and Cook would almost certainly have upset under two or three thousand more kgm., and it is the experience of the author that it is difficult to obtain even steel washers which will stand much more than 8000 kgm. without taking some set. In fact, at high pressure there must necessarily be some plastic yield, in order to follow the expansion of the cylinder. The result of this set in the washers is that the friction becomes very irregular, and cannot be assumed to be the same during increasing and decreasing pressure. Variations in the amount of friction due to this cause of as much as 200 or 300% have been found at the higher pressures of this work.

The only escape from the difficulty seems to be to measure the pressure directly inside the cylinder. This was done by Tammann by connecting a Bourdon gauge directly to the cylinder. But it is known that the errors of the Bourdon gauge become rapidly more serious at higher pressures,[4] due to the increase of hysteresis, so that this gauge could not be used for the pressures of this experiment. Furthermore, no Bourdon gauge has up to the present been made of sufficient sensitiveness which is capable of standing more than 6500 kgm. In the present work the pressure was measured inside the cylinder by inserting directly into it a coil of manganin wire, which had been already calibrated against an absolute gauge. This method of measuring pressure has been fully described in a previous paper.[5] It was necessary for the purposes of the present work, however, to make a somewhat more careful determination of the temperature coefficient than was done formerly, and this determination will be described in detail later. The method has shown itself perfectly satisfactory and reliable in every respect. One coil of wire has been used almost continuously for over six months, and occasional calibrations have shown no change. These calibrations were made by measuring with the coil certain fixed temperature-pressure points, such as the freezing pressure of mercury or of ice VI, at some fixed temperature.

The apparatus used in the present work is the same in most features as that used in the former work, a detailed account of which has already been given in the papers mentioned. Only the points in which this has been changed will be mentioned here. It was a disadvantage of the former method that the apparatus consisted of two parts; the lower part, a cylinder containing the liquid to be measured, was placed in a thermostat, and the upper part, a cylinder in which pressure was produced, was exposed to the temperature of the room. When temperature was changed in the thermostat below or pressure was changed in the cylinder above, liquid passed from the one cylinder to the other, experiencing in the transition a change of temperature, and so a change of volume also. This change of volume accompanying a known change of temperature varies in an unknown way with the pressure, and to apply the correction it was necessary to make an independent set of experiments. In the present form of apparatus the difficulty was avoided by including everything in one cylinder. This cylinder contained the liquid under investigation, the pressure measuring coil, and the piston by which pressure was produced. It was placed in the lower part of the hydraulic press and, together with the lower part of the press, was placed in the thermostat. The dimensions were so small that this could be done without increasing to an unwieldly bulk the size of the apparatus, the four tie rods of the press being 1 1/8″ in diameter and their centers 6″ apart. It is the same form of apparatus which was used for the measurements on ice VI up to 20,500 kgm. The present experiments run to only 12,000 kgm., however, since it is evidently an absolute essential to the success of the method that there should be no permanent distortion of the cylinder. It would be easily possible to reach pressures much higher than those reached in this experiment, but it was felt that the risk and the extra time involved in the probable construction of new apparatus was not justified at present, when it seemed that the most important work was to map out the field, obtain data for as many liquids as possible, and determine the general nature of the significant problems. Later, if there are crucial points which need the use of much higher pressures, it will be a comparatively easy matter to obtain them.

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[4] Bridgman, These Proceedings, **44**, 201–217 (1909).

[5] Bridgman, These Proceedings, **47**, 319–343 (1911).

The cylinder used in this experiment was not the same as that used in the previous work on water. This new cylinder is from a piece of chrome-vanadium steel made in the electric furnace by the Halcomb Steel Co., of Syracuse, N. Y. The steel itself is a wonderful product, and without it the present investigation would not have been so easily possible. It shows a tensile strength of 300,000 lbs. per sq. in. when hardened in oil, and an elastic limit of about 250,000 lbs. These figures are considerably in excess of those for the steel used in the previous investigation. The steel furthermore is remarkably homogeneous, because of its production in the electrical furnace. One of these pieces was pierced with a hole 1/8″ diameter and 13″ long, and the drill came through concentrically without any variation from the straight line. The dimensions of the cylinder used in the present work were 4 1/2″ outside diameter, 13″ long, inside diameter 17/32″ for the greater part of its length, with an enlargement to 3/4″ at the lower end for the reception of the manganin coil. The original inside diameter was 7/16″. The cylinder was prepared for use by hardening in oil and then subjecting to a pressure much in excess of that contemplated for the actual experiment. The seasoning pressure was over 30,000 kgm. Even under this high seasoning pressure the cylinder showed very little permanent change of internal dimensions, not stretching as much as 1/32.″ This is less than the amount of stretch which has been found for any other grade of steel. The effectiveness of the treatment is shown furthermore in the fact that in over six months of continual use the inside has not stretched by so much as an additional 1/10000″. The hole was enlarged to a final size of 17/32″, instead of keeping it as small as possible, because of the difficulty of reaming out the hole so as to give a satisfactorily smooth surface after the seasoning process. The difficulty was occasioned by the hardness of the steel, and several attempts were necessary before the desired result was produced.

The pressure measuring coil was the same as that used in the last part of the work on ice VI. The construction of the insulating plug was also the same as that used there. During the course of the work it was necessary to take this plug apart several timess, because water had reached the mica washers, and once or twice the mica washers themselves have given way. These mica washers are the weakest part of the entire apparatus as at present used, since they gradually disintegrate and fail by shear after prolonged use, but it is a matter of only a few hours to replace them. Every time after the insulating plug has been freshly set up it has been tested for insulation resistance, both during application of pressure and after release. The resistance was in all cases as high as several hundred megohms, the limit of the measuring devise. The steel of the insulating plug has also failed once or twice by the "pinching-off effect" [6] after long use. This also is an easy matter to repair. Failure of this type is attended with some danger, however, because of the violence of the explosion with which the ruptured plug is expelled. The surest way of avoiding this danger is to so mount the apparatus that the plug points at the floor or other indestructible object.

The hydraulic press, the method of measuring the displacement of the piston, and the details of the packing of the moving piston, were the same as that used in the former paper.

In the use of the apparatus to determine compressibility there is one serious error which did not enter into its use in the determination of the change of volume during change of state, namely the correction for the distortion of the cylinder in which the piston moves. At low pressure the correction is relatively unimportant, and may be computed from the theory of elasticity, if one is willing to assume that the theory is sufficiently accurate for this type of stress. But at higher pressures the correction becomes more important, increasing in percentage value directly with the pressure, and is almost certainly not calculable by the theory of elasticity, because of the entrance of such effects as hysteresis. To determine the correction an auxiliary set of experiments is necessary. Evidently if the true value of the compressibility of some one substance were sufficiently well known, then the apparent compressibility as determined by this method would give the correction for the distortion of the cylinder. No such compressibilities are known with any high percentage accuracy, but this is not necessary, provided only that the uncertainty in the standard compressibility is small in comparison with the distortion of the vessel. The substance which most readily suggests itself because of its small compressibility is steel, but this is a solid, whereas the method is applicable directly only to liquids, so that some modification of the procedure is necessary. Such a modification readily suggests itself, and has been used by the author in the previous determinations of the thermal dilatation of water at temperatures below 0°, and has also been used by Parsons and Cook. The modification is to replace part of the liquid under investigation by a steel cylinder, and determine the compressibility of the liquid and the steel together. The difference of two determinations, the one for the liquid alone, the other for the liquid and the steel, gives a value for the difference of compressibility between the liquid and the steel from which the effect of the distortion of the vessel has been almost entirely eliminated. Furthermore, the compressibility of the steel is so small in comparison with that of the liquid that the slight uncertainty in the value for the steel is of no account, so that the compressibility of the liquid is given directly.

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[6] Bridgman, Phil. Mag., **24**, 63–79 (1912).

The application of this method would demand, then, that the interior of the cylinder be filled first with water and the apparent compressibility determined, and then part of the water replaced by steel and the apparent compressibility determined again. But this demands that the coil of manganin with which the pressure is to be measured come directly in contact with the water, which evidently cannot be allowed because of the short circuiting produced by the water. It seemed to be necessary, then, to devise some sort of protection for the coil, which should not occupy so much volume as to introduce a serious correction, and which should at the same time transmit the pressure readily to the innermost parts of the coil. Considerable time was spent in trying to devise such a protection. The scheme adopted was to surround the coil with a small mass of vaseline enclosed in a flexible sac, formed from the finger of a silk glove, and rendered impervious to water by painting it over with several coats of the collodion of surgeons. This sac was tied with silk thread directly over the end of the insulating plug. It was proved by trial that the vaseline did not become so viscous under pressure as to refuse to transmit the pressure with sufficient freedom, but the arrangement did not prove itself as trustworthy as was to be desired. The collodion might leak after several applications of pressure, which made it necessary to reassemble the insulating plug and redetermine the elastic constants of the apparatus, because the distortion included in the plug itself was sufficient to introduce appreciable error. The device probably could have been made usable with a little more effort, but it would always have been more or less unsatisfactory, and would have been applicable only to those liquids which do not attack the collodion, whereas most of the organic liquids which it was desired to use in the future do so attack the collodion. The attempt to protect the coil was abandoned after a month's work, therefore, and the method replaced by another, which at first sight introduced additional complications, but which is really just as simple as the first, and has the advantage of being applicable with only slight modifications to the investigation of other liquids.

The modified method used two liquids in every determination, one beside the one whose compressibility is to be measured. The water under investigation is placed in a thin shell of steel fitting the inside of the cylinder. This shell, when in position in the cylinder, is surrounded on all sides and above and below by kerosene, which below transmits pressure to the manganin coil, and above reaches to the moving piston with which pressure is produced. In the auxiliary experiment to eliminate the effect of the distortion of the cylinder, the shell with water is replaced by a solid cylinder of steel, and the quantity of kerosene remains the same as before. The motion of the piston due to the change of volume of the kerosene remains the same in the two experiments, therefore, and the difference of readings of the two sets gives directly the difference of compressibility between the water and the steel. The disadvantage of the method is that it is not possible to use so large quantities of water as in the former method, because the steel shell containing the water remains invariable in length under pressure, and enough kerosene must be introduced originally to take up the change of volume of the water in this shell as well as the distortion of the other parts of the apparatus. The reduction in the quantity of water under experiment is not greater than 30%, however, and the other advantages more than outweigh this comparatively small loss of accuracy.

The procedure in using the apparatus in this finally modified form is as follows. The manganin coil is first screwed into the lower part of the cylinder. The rubber washer used to make this plug tight is one cut with a standard set of cutters, so that all the washers used for this purpose are always the same in size. This insures that the distortion due to the compression of the washers shall always be the same. The steel shell with the water in it is next introduced from above. The quantity of water is previously determined by weighing. It is desirable not to fill the shell to closer than 1/4″ of the top, experience having shown that otherwise water is likely to spill out and find its way to the manganin coil. The kerosene is next introduced into the cylinder from above. To ensure entire filling of all parts of the apparatus and the exclusion of air, only part of the kerosene is at first poured in, the air is then exhausted by attaching the mouth of the cylinder to an air pump, or simply by exhausting with the lungs, and then the remainder of the kerosene poured in. The amount of kerosene is determined by weighing the dish from which it is poured before and after filling. Because of the wetting of the dish by the kerosene it is not always possible to obtain exactly the amount of kerosene desired each time, but the variation is seldom over 0.02 gm., and the very slight effect of this discrepancy may be corrected for, as will be described later. Finally the movable plug is introduced into the top of the cylinder, taking particular pains not to allow any of the kerosene to escape in the process. Here again the rubber washer used has been cut with standard cutters, so that the amount of rubber used here is also the same in all the experiments. The cylinder is then placed in the thermostat, and the zero of the manganin coil read at the temperature of the room. The thermostat is then adjusted for the desired temperature and the cylinder seasoned for the run by the application of pressure.

A preliminary seasoning is necessary because of the hysteresis shown by the cylinder, and this hysteresis is shown with respect to both pressure and temperature. Many of the early results were somewhat in error because the necessity of this seasoning for temperature as well as for pressure was not clearly recognized. The method of seasoning to be adopted depends on the kind of data which it is desired to obtain from the run, whether the compressibility at constant temperature or the thermal dilatation at constant pressure. If it is desired to determine the isothermal compressibility, the seasoning consists simply in raising the pressure through the entire range and releasing several times. It was found by experiment that three such preliminary excursions were sufficient; after this the cylinder settles down into a state in which the normal hysteresis cycles are retraced with perfect regularity. Of course it is necessary to make the compressibility determinations immediately after this seasoning, as the effect gradually disappears with time. The time occupied in making the final readings to 12,000 kgm. and back with increasing and decreasing pressure, making in all 20 readings, might vary from two to three hours. After every change of pressure it was necessary to wait for the temperature effect of compression to disappear; this time was from 5 to 7 minutes.

If the thermal dilatation under constant mean pressure is to be determined, the seasoning consists simply in taking the cylinder once through the temperature range contemplated as well as through the pressure range. A word of description as to the general procedure in determining the thermal dilatation at constant mean pressure will not be out of place. The general plan is to change the temperature while the piston is kept invariable in position, and therefore while the volume is also approximately constant. The rise of temperature produces a rise of pressure, so that after the rise of temperature it is necessary to bring the pressure back to the former value by withdrawing the piston if the change of temperature has been an increase, or advancing it if the change of temperature has been a decrease. The amount by which the piston is withdrawn, as also the new final pressure, is noted. The temperature is then changed again, and the same set of readings made again. Thus every observation at any given temperature involves two readings of the position of the piston and the corresponding pressure. The slight change of pressure during the changes of temperature carries with it hysteresis effects, which it is necessary to avoid by previous seasoning, exactly as for pressure changes over a wider range. Two processes of seasoning are necessary for temperature, therefore, one a larger one for the entire temperature range, and another smaller one for the slight changes of pressure incident to the changes of temperature. This second seasoning is made after the first more extensive seasoning simply by running the pressure back and forth several times through the small range of pressure to be met with during the temperature changes. This small range was determined by preliminary experiment.

In the actual calculation of the results there are a number of corrections to be applied. These will now be discussed in detail separately. In the first place the temperature coefficient of the manganin coil has to be determined with particular care. This is because the pressure changes brought about by changes of temperature during the determinations of the thermal dilatation are comparatively slight, so that any change of the pressure coefficient of the coil brought about by the change of temperature appears in the result greatly magnified. Thus for the sake of example, we will suppose that a change of temperature of 20° produces a change of pressure of 400 kgm. at 10,000 kgm. total pressure. This figure is a fair average of the results to be met with in practice. If now the pressure coefficient of the coil is changed by 1% by this same rise of temperature, the pressure will thereby appear to have risen 500 kgm. instead of the actual 400, introducing an error of 25% for a change in the constant of the coil of only 1%. In addition to the effect of the temperature coefficient of the coil, there is an effect due to the change of the zero of the coil with temperature, but this change can be determined by observations of the temperature coefficient of the coil at atmospheric pressure and is easy to measure with the requisite accuracy.

The change in the pressure coefficient of the coil with temperature is more difficult to determine with the desired accuracy. It would not be possible to determine this by a direct calibration against the absolute gauge with which the mean value of the coefficient has been determined, for the reason that the absolute gauge itself is not accurate to better than 1/10%, and this would still leave a possible error in the thermal dilatation of 2.5%. To affect the desired calibration, some standard of pressure must be used which can be relied on to remain absolutely constant. Such a standard pressure is evidently afforded by the transition point of the liquid to the solid form of any convenient substance at some fixed temperature. In previous work the transition points of both water and mercury have been determined at various temperatures with an accuracy in the absolute pressure of 1/10%. To make the calibration it is only necessary to keep the pressure constant automatically at this known value by placing in communication with the chamber in which is the manganin coil to be calibrated another chamber in which are the liquid and solid forms of the substance whose transition temperature and pressure are known. This second chamber is to be kept at constant temperature accurately enough so that slight changes in this temperature will not produce changes of more than the allowed amount in the transition pressure. For this purpose the most convenient fixed temperature seems to be that of melting ice at atmospheric pressure, and the most convenient substance to use mercury, because of the sharpness of the freezing, and the ease with which it can be obtained pure.

The actual arrangements in making this calibration for the temperature coefficient of the pressure coefficient of the coil were as follows. The upper cylinder of the hydraulic press in which pressure was produced contained in addition to the moving plunger a steel shell in which was as large a quantity of mercury as convenient, about 150 gm. This upper cylinder as well as the entire lower part of the press was surrounded by a tank containing ice and water, by which the temperature of the mercury could be kept continuously and accurately at 0°. A heavy nickel steel tube led out of the lower end of the upper cylinder through the bottom of the tank, and connected with the lower cylinder in which was the manganin coil under examination. This lower cylinder was placed in an oil bath with thermostatic regulation, by which the temperature could be set at and retained at any desired value. The experimental procedure was as follows. The temperature of the lower bath was set at any desired value, and the pressure increased until the freezing point of mercury at 0° was slightly passed. The mercury then froze with decrease of volume, thus bringing the pressure back to the known equilibrium value at 0°. After equilibrium had been reached, the resistance of the manganin coil was read. The pressure was then lowered slightly by withdrawing the piston. This was followed by automatic restoration of the equilibrium pressure, brought about by melting of the frozen mercury with increase of volume. The transition point was always so sharp that no difference could be detected in the equilibrium pressure whether approached from above or below. The temperature in the lower cylinder containing the manganin was then changed to another desired value. This change of temperature, if it were an increase, would naturally carry with it a rise of pressure, but the pressure is then automatically lowered by the freezing of the mercury. After a steady state is reached, the new value of the manganin resistance is read, and then the pressure lowered again by slightly withdrawing the piston, and the value of the resistance noted again after the equilibrium conditions have been restored from below. In this way the coil can be calibrated over the entire temperature range contemplated for the experiments. Of course this calibration is good only for one fixed pressure, but in view of the proved linearity of the pressure-resistance relation within 1/10% from 0° to 50°, it seemed safe to let the calibration go at this one determination, particularly since no effect could be found.

The calibration of the manganin was carried out at five temperatures; 25°, 45°, 65°, 85° and 110°. No appreciable change of the coefficient could be found for the four lower temperatures, but between 85° and 110° there is a very perceptible change of 1%. But since the range of temperature of the actual experiment did reach over 80°, no correction was applied to the observations for this effect. It is to be noticed that this result is valid only for this one coil, since previous work, both by Lisell [7] and by the author, have shown that different pieces from the same spool of wire may show slight variations in the temperature coefficient, which is sometimes positive and sometimes negative.

In addition to this special calibration for slight relative changes in the pressure coefficient with temperature, the absolute value of the pressure coefficient has been checked from time to time during the course of the experiments. This could be done conveniently with the apparatus as used for the compressibility determinations by determining the transition point of ice VI, or of mercury at known temperatures. These calibrations have shown no change whatever in the pressure constant of the coil.

It has already been stated that the actual measurements involve two sets of readings, one with the apparatus filled with water, kerosene and a small amount of bessemer steel, and a second set with additional steel replacing the water. By subtracting the piston displacement at any given pressure for these two sets of experiments a value is obtained which gives approximately the piston displacement for the water alone, and from which the effect of the distortion of the vessel has in large measure been eliminated. But a moment's consideration will show that the effect of distortion has not been entirely eliminated, and it is necessary to apply a correction for the slight residual effect. The correction comes because of the fact that the position of the piston at corresponding pressures is not the same in the two sets of experiments, so that the subtraction leaves still uncorrected the distortion due to the part of the cylinder exposed to pressure in the one set of experiments and not so exposed in the other. This correction cannot be determined directly, and the only way seems to be to calculate it by the ordinary theory of elasticity, taking for the constant of the steel the values under ordinary conditions, which are known not to vary much even for the most different varieties of steel. There is undoubtedly some error in the correction as so determined, but the total value of the correction is at best small, and any such error is relatively unimportant.

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[7] Lisell, Om Tryckets Inflytande på det Elektriska Ledingsmotståndet hos Metaller samt en ny Metod att Mäta Höga Tryck (Diss. Upsala, 1903).

The compressibility of the steel replacing the water also evidently enters as a correction factor. This compressibility is relatively slight, and it has been previously determined over a range of 10,000 kgm. The value of the compressibility of the steel also changes with the temperature, but this change has also been shown by direct experiment to be slight, so slight that it can be neglected. In the present work the value was assumed to be constant, independent of temperature and pressure, having the value 58×10^{-8} per kgm. per sq. cm.

There is also a correction to be applied for the compressibility of the kerosene, if the amount does not happen to be the same in the two sets of experiments, and it was seldom that the amount was exactly the same. The variation was very small, however, and the correction is easy to apply if the compressibility of the kerosene itself is known. This was determined with sufficient accuracy for the purpose by an independent set of experiments, exactly the same in principle as those for determining the compressibility of water. The results of these independent experiments are given at the end of the paper.

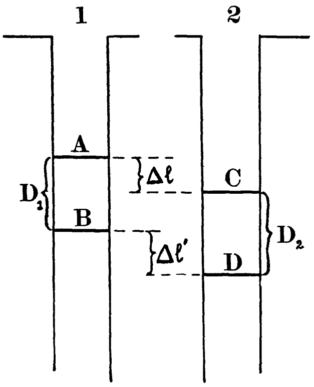

FIGURE 1. Diagram showing the position of the piston. To go with the computations for the corrections to be applied to the compressibility.

The following formulas were used in making the corrections, and include all the corrections mentioned qualitatively above. Figure 1 shows the position of the piston at different times in the course of the experiment. The left hand part of the diagram (denoted by the suffix 1) is for the cylinder when it is filled with kerosene and bessemer steel only, and the right hand part (denoted by the suffix 2) is for the cylinder when it contains water, kerosene, and bessemer steel. A and C are the positions of the piston at the arbitrary zero of pressure in these two sets of experiments (this arbitrary zero was usually taken in the neighborhood of 2000 kgm. and will be denoted by p), and B and D indicate the position at some higher pressure, the same in the two sets, which will be denoted by p'. We now write down the expressions for the total volume of the cylinder beneath the piston.

$$\begin{aligned} \text{At A, } V_1 &= V_{1k} + V_{1s} \\ \text{At B, } V_1' &= V_{1k}' + V_{1s}' \\ \text{At C, } V_2 &= V_{2k} + V_{2\,H_2O} + V_{2s} \\ \text{At D, } V_2' &= V_{2k}' + V_2'{}_{H_2O} + V_{2s}' \end{aligned}$$

where the suffixes K, H_2O, or S indicate that the volume is for the kerosene, the water, or the steel respectively.

Subtracting the equations above from each other, we obtain

$$(V_1 - V_2) - (V_1' - V_2') = (V_{1k} - V_{1k}') - (V_{2k} - V_{2k}') \\ - (V_{2\,H_2O} - V_2'{}_{H_2O}) + (V_{1s} - V_{1s}') - (V_{2s} - V_{2s}').$$

We now denote by Δl the difference of displacements at the two positions A and C, and by $\Delta l'$ the corresponding difference at the positions B and D. We now assume that V_1 and V_2 differ only by the volume of the cylinder of length Δl, and similarly V_1' and V_2' differ only by the cylinder of length $\Delta l'$. This assumption is justified if only the positions of the pistons at A and C are so far removed from the end of the cylinder that the end effects in the distortion of the interior are the same in the two cases. This condition has been shown by the theory to be satisfied when the distance is two or three diameters, as it always was in these experiments. Hence we may write,

$$\begin{aligned} V_1 - V_2 &= s_0\,(1 + a\,p)\,\Delta l \\ V_1' - V_2' &= s_0\,(1 + ap')\,\Delta l', \end{aligned}$$

where s_0 is the initial section of the cylinder at atmospheric pressure, and a is the factor of proportionality by which this is changed with pressure. Now if we call the displacement form A to B, D_1 and from C to D, D_2, then

$$D_2 + \Delta l = D_1 + \Delta l'$$

and the above equation may be thrown into the form

$$V_1 - V_2 - (V_1' - V_2') = - s_0(D_2 - D_1)\,(1 + a\,p') + s_0\,\Delta l a\,(p - p')$$

We now make use of the fact that the total change of volume of any substance under pressure is proportional to its mass. If $\Delta\, v$ (positive for a decrease) is taken as the change of volume of 1 gm. between p and p', then,

$$\begin{aligned} V_{1k} - V_{1k}' - (V_{2k} - V_{2k}') &= \Delta\, v_k\,(m_{1k} - m_{2k}) \\ V_{2\,H_2O} - V_2'{}_{H_2O} &= \Delta\, v_{H_2O}\, m_{H_2O} \\ (V_{1s} - V_{1s}') - (V_{2s} - V_{2s}') &= \Delta\, v_s\,(m_{1s} - m_{2s}) \end{aligned}$$

This enables us to solve the equations for the compressibility of the water and the kerosene, giving,

$$\Delta v_{H_2O} = \frac{1}{m_{H_2O}} \{ s_0 (D_2 - D_1)(1 + \alpha p') - s_0 \Delta l \alpha (p - p') \\ + \Delta v_k (m_{1k} - m_{2k}) + \Delta v_s (m_{1s} - m_{2s}) \}$$

and for the kerosene, when the two runs are both made with kerosene, as in determining the data for kerosene given at the end of the paper,

$$\Delta v_k = \frac{1}{m_{2k} - m_{1k}} \{ s_0 (D_2 - D_1)(1 + \alpha p') - s_0 \Delta l \alpha (p - p') - \Delta v_s \\ (m_{2s} - m_{1s}) \}$$

The considerations so far apply only to the measurement of compressibility at constant temperature. The thermal dilatation is determined in the same way as the compressibility from the difference of the thermal dilatation as given by two sets of experiments, one with the water replaced by steel. The piston displacement is not the same at corresponding pressures here, either, and a correction is to be applied for the thermal dilatation of the part of the cylinder which is exposed to pressure in the one experiment and not so exposed in the other. But this portion of the cylinder to which the correction is to be applied was seldom more than 1″ in length, and the correction for this amount of steel is negligible in comparison with the thermal dilatation of the total quantity of water. There is also a correction to be applied for the dilatation of the steel replacing the water, and this correction is small but not negligible. It was assumed that the dilatation of the steel remains independent of the pressure over the pressure range used, and the value for ordinary mild steels at atmospheric pressure was employed. This value is 0.000039 for the cubic expansion per degree Centigrade.

The corrections to the measurements of the thermal dilatation are not so serious or so important as those for the compressibility, since the total effect is much smaller and most of the corrections become negligible. The method of determining the thermal dilatation has already been explained to be that of observing the change of pressure brought about at constant volume by a known change of temperature. From this the change of volume with temperature at constant pressure can be immediately determined if the slope of the p-v curve at that point is known, for $\left(\frac{\partial v}{\partial \tau}\right)_p = -\left(\frac{\partial v}{\partial p}\right)_\tau \left(\frac{\partial p}{\partial \tau}\right)_v$. $\left(\frac{\partial v}{\partial p}\right)_\tau$ is evidently given directly from the curves for compressibility at constant temperature. The slope of this curve changes somewhat with the temperature, so that a correction should be applied for this, but the change is so slight at the higher pressures that for this purpose the compressibility can be assumed constant. At the lower pressures, below 2500 kgm., the change cannot be neglected, and another method of computation must be applied.

The thermal dilatation at low pressures was determined by taking directly the difference between the isothermals traced out at different temperatures. This method is not applicable at high pressures because the irregularities of isothermals traced at different times is sufficient to make their difference an inaccurate measure of the slight change of volume with temperature, but at the low pressures, the errors introduced by hysteresis and other irregular action of the steel cylinder are so slight that the method may be used directly to give the value of the compressibility, and by taking the differences, the value of the thermal dilatation. In fact it would seem that the method would be applicable with slight modifications to the determination of the compressibility of a great variety of substances at low pressures, and it is very much more rapid than the methods hitherto used.

A special setting up of the apparatus was necessary for the experiments at low pressures, because in order to be able to reach low pressure on release of pressure it is necessary that the friction in the movable plug be not too high, and if the pressure has once been run to so high a value as to upset the plug, the friction becomes so great as not to permit release of pressure to much below 1500 kgm. For these experiments, then, the plug was made initially a push fit for the hole, by making it about 0.0015″ smaller than when used for the higher pressures, and in performing the experiment the pressure was never pushed beyond 2500 kgm. In other respects the experiments at low pressures were the same as those at higher pressures. It was not necessary to take quite so elaborate seasoning precautions at these low pressures, however.

With regard to the amount of hysteresis or elastic after-effects to be met in the experiments, the difference of the displacment with increasing or decreasing pressure usually amounted at the middle of the range to 0.03 in. This amount was very uniformly consistent, indicating that the cylinder had really settled down to a steady behavior. The piston always returned to the starting point to within the limits of accuracy of reading, indicating that there was no leak or permanent set, or wearing of the packing in appreciable amount.

Of course the experiments at low pressures showed very much less hysteresis, in fact it was so small as to be almost imperceptible. The effect of hysteresis was eliminated as far as possible by using for the displacement at any pressure the mean of the results with increasing and decreasing pressure. The hysteresis was so constant that it would probably have been sufficient to have used consistently the results either at increasing or decreasing pressure. The actual procedure has, therefore, the weight of two independent determinations. In the determinations of thermal dilatation, on the other hand, the hysteresis effects were so much smaller, that except for one run initially to show that there was no effect of this kind, the readings were always made either only with increase or only with decrease of temperature for any mean pressure, never with both increase and decrease.

The Data.

Three independent sets of experiments were performed to give the change of volume with temperature and pressure over the entire range; namely the isothermal compressibility at pressures over 2500 kgm., the isothermal compressibility and the thermal dilatation at pressures below 2500 kgm., and the thermal dilatation at pressures over 2500 kgm. This is the actual order of experiment, but for the purposes of presentation it will be better to use the natural order, proceeding from low to higher pressures.

Compressibility at Low Pressures.

The method with the present form of apparatus is not very sensitive at the low pressures, and not many measurements were made over this range. Two sets of determinations of compressibility were made, the first at 20°, 40°, 60°, and 80°, and the second at only 20° and 80°. Here, just as for the measurements at the higher pressures, there is always sufficient friction in the packing after the pressure has once been applied not to permit of close enough approach to the zero to make an extrapolation back to the zero justifiable. And if the extrapolation to the zero is to be made from the readings during first application of pressure, special effort has to be made to design the washers so as to avoid small initial distortions. For this reason only the second of the above sets could be used by extrapolation back to the zero of pressure. The readings of volume at 20° and 80° were corrected back to 40° from the thermal dilatation as determined by this same set of experiments, so that we have from the above two values for the compressibility at 40° up to 2200 kgm. The first set of readings at five temperatures is consistent with this latter set above 1000 kgm., but at the lower pressures gives values for the compressibility which are doubtless too high. To find the best value for the change of volume at low pressures we now have three sets of data, those of the present determination, those of the previous work by the method of the steel piezometers, and the results of Amagat. The most probable value for the change of volume has been found by comparing these three sets of values. These values are given in Table I, as also the mean selected from them as the most probable value from the data at present in hand. In taking this mean, the greater weight has been given to the values of Amagat at the lower pressures, since his method of measurement was doubtless more accurate for the low pressures than the present method, which was intended only for high pressures, but at the upper end of the range in the neighborhood of 2000 kgm., more weight has been given to the present determinations. It is to be noticed that the mean value taken as final is lower than that found by Amagat. This divergence is in the same direction as that found by Parsons and Cook, who worked with a method like the present one. The deviation found by them from the results of Amagat is greater than that adopted here.

TABLE I.

VOLUME OF WATER AT 40° AND LOW PRESSURES BY DIFFERENT METHODS.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$	Change of Volume, cm.^{3}/gm.			
	Steel Piez.	Piston.	Amagat.	Fina Mean.
0	.0000	.0000	.0000	.0000
500	.0200	.0202	.0204	.0203
1000	.0368	.0377	.0378	.0376
1500	.0527	.0527	.0534	.0532
000	.0669	.0667	.0676	.0673

Dilatation at Low Pressures.

For the thermal dilatation at low pressures, two sets of determinations were made; one was the series of isotherms at four different temperatures already mentioned, and the second was by the method adopted for the higher pressures, namely variation of temperature at constant mean pressure. The method of calculation for this lower range was not the same as that employed for the higher pressures, as already explained, due to the fact that the slope of the isothermals is not sufficiently independent of temperature at the lower pressures. The method of computation adopted here was a graphical one, by plotting the observed volume and pressure points for the different temperatures and taking the difference between adjacent curves graphically. The temperatures at which the different determina-

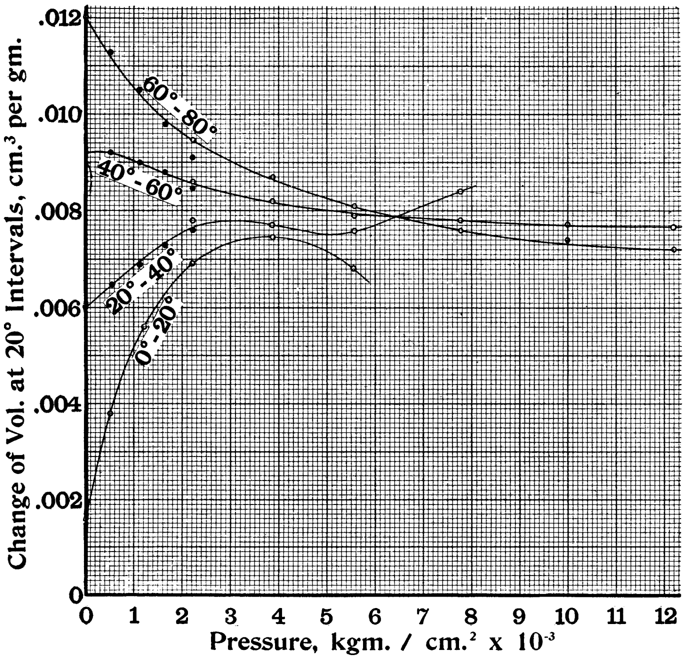

Figure 2. The change of volume of water for intervals of 20° plotted against pressure.

tions were made were not exactly the even temperatures desired, namely 20°, 40°, and 60°, and 80°, but they were in all cases within a few tenths of a degree of these temperatures. The results were corrected to these even temperatures by assuming the mean variation with temperature over the whole temperature range to hold for the few tenths of a degree on either side. The final result given by the data is the total change of volume for an interval of 20°; from 20° to 40°, from 40° to 60°, and from 60° to 80°. The mean of the results of the two sets of experiments is shown with satisfactory accuracy in Figure 2, on which are plotted all the values obtained by the different methods. The results for the low pressures are shown in the full black circles. These values are seen to extrapolate, without forcing, to the values already found by other observers for atmospheric pressure, and they also make fairly good connections with the values found by the other method for the higher pressures. In view of this agreement it did not seem to be necessary to make further determinations of this quantity.

Compressibility at High Pressure.

The determinations of the isothermal compressibility at higher pressures extended over a considerable interval of time and are more numerous than any of the other determinations. In all, twelve determinations of this quantity were made, at five different temperatures. These determinations include those made during the early course of the experiment, when the attempt was being made to find the thermal dilatation directly from the difference of compressibility at different temperatures. A little work with the method showed that it was not sufficiently accurate for the purpose, but the results obtained then can be used to give the compressibility at the standard temperature, 40°, by applying the temperature correction found from the later more accurate results. The temperature of 40° was chosen as the standard because this is the lowest of the 20° intervals at which the water is liquid up to 12000 kgm.

The results of these twelve determinations, extending over a period of three months, are shown in Table II. The results as given are reduced to 40°, but the temperature at which the original measurements were made is given also in the table. Two of these sets of determinations differ considerably from the others, and were discarded in taking the mean, although as it happens one of these discarded sets is too high and the other too low, so that it makes very little difference

TABLE II.

Results of Different Determinations of Change of Volume of Water at 40°.

Pressure, kgm./cm.^{2}	Change of Volume, cm.^{3}/gm.												
	Jan 22–27.	Dec. 19–29.	Dec. 4–6.	Nov. 29-Dec. 1.	Nov. 27–28.	Nov. 24–25.	Nov. 9–10.	Nov. 8–9.	Nov. 6–8.	Nov. 3–4.	Nov. 2–3.	Nov. 1–2.	Final Mean.
2220	.0000	.0000	.0000	*.0000	.0000	.0000	.0000	*.0000	.0000	.0000	.0000	.0000	.0000
3330	.0255	.0256	.0266	.0268	.0255	.0262	.0257	.0243	.0260	.0253	.0256	.0250	.0257
4440	.0471	.0476	.0487	.0494	.0473	.0481	.0468	.0452	.0471	.0465	.0472	.0466	.0473
5550	.0656	.0666	.0675	.0687	.0660	.0670	.0652	.0635	.0650	.0648	.0658	.0652	.0659
6670	.0816	.0830	.0836	.0852	.0820	.0830	.0813	.0794	.0806	.0809	.0818	.0810	.0819
7780	.0956	.0974	.0979	.0999	.0962	.0970	.0956	.0937	.0947	.0953	.0961	.0952	.0961
8890	.1079	.1100	.1100	.1126	.1087	.1094	.1086	.1064	.1072	.1083	.1088	.1077	.1087
10000	.1190	.1211	.1213	.1238			.1201	.1178	.1186	.1198	.1201	.1189	.1199
11110	.1291	.1310	.1313	.1337			.1305	.1282	.1291	.1302	.1304	.1289	.1301
12220	.1386	.1398					.1412	.1377			.1413	.1408	.1403

* Discarded in taking mean.

in the final result whether they are included in the mean or not. For convenience in making the computations the pressure was taken in units given conveniently by the changes of the manganin resistance, the intervals of pressure corresponding to a displacement of the slider of the bridge wire of 5 cm.

TABLE III.

COMPARISON OF RESULTS BY TWO METHODS FOR CHANGE OF VOLUME OF WATER AT 20°.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$	ΔV.		Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$	ΔV.	
	Piston.	Piezometer.		Piston.	Piezometer.
2220	.0000	.0000	6670	.0814	.0821
3330	.0257	.0259	7780	.0954	.0964
4440	.0472	.0479	8890	.1078	.1105
5550	.0659	.0666	10000	.1190	.1229

These results, reduced to 20° are shown compared with the results of the previous determination in Table III. It is seen that the newer results are lower than the former ones, the difference being about 1%, except at the higher pressures, where the difference is greater. The agreement is perhaps not as close as could be desired, but at present there seems to be no way of choosing between the results. There is no consistent discrepancy, which would indicate a fundamental error in the present method, such as in the correction applied for the distortion of the steel cylinder, for example. If there were any such error it could be eliminated by so choosing the correction as to make the present results agree with the former ones. In the absence of any means of deciding between the two methods therefore, and since the results by the present method reach over a wider temperature and pressure range, and since also the method has been used much more extensively than the former one and with no greater discrepancy in the individual results, these present results have been accepted as the best ones. But it must be remembered that the absolute compressibility given here may be in error by as much as 1% at the higher pressures. This error, however, will not be found to invalidate any of the conclusions drawn from the data.

Dilatation at High Pressures.

The determinations of the thermal dilatation at the higher pressures were made on four occasions. The first two of these were preliminary, during which was discovered the necessity of seasoning for temperature as well as for pressure, and also the necessity for the secondary pressure seasoning over the small range of pressure accompanying the changes of temperature. These first two determinations, while confirming the results of the two later ones, were not given much weight in selecting the final value. The method of computation adopted in finding the thermal expansion from the data requires mention. At first an attempt was made to apply the same graphical method which has been already explained in its application to the determinations at the lower pressures. This method involves the drawing of a curve of the same general slope as the compressibility curve through the two points giving piston displacement against pressure at each temperature. But it was found that even after the seasoning for the small pressure range involved here, the points were too irregular to give good results by this method. The irregularities may be due to residual hysteresis, but are more probably due to slight irregularities brought about by the motion of the piston itself. These irregularities are too minute to have any effect on the compressibility determinations. The best way to avoid them is to utilize in the computations only those readings during which the piston remains stationary. This means that only the change of pressure accompanying a change of temperature is used in making the computations, the second reading at any temperature by which the pressure is brought back to the mean value being ignored. The change of volume at constant pressure for the given change of temperature is then computed from the known change of pressure at constant volume and the previously determined change of volume with pressure at constant temperature. In making this computation it is generally necessary to make two corrections; one to bring the temperature interval to the exact 20° desired for the final results, and the second to correct for the very slight change of measured piston displacement accompanying the change of temperature. This change of displacement is seldom over 0.003″. It is probably not due entirely to actual motion of the piston, but partly to temperature changes in the bars of the press which dip into the thermostat. That this method of computing the results is preferable to the graphical one previously mentioned is shown by the fact that this method gives very much more uniform and consistent results when applied to the same set of data than the graphical method.

The method of computation adopted was first to calculate independently from the individual observations of each set of readings the thermal dilatation at six mean pressures between 2200 and 12,000 kgm. Then smooth curves were drawn through these points for each set of readings, the curves being spaced in the best way so as to give regular variations with both pressure and temperature. The values given by the smooth curves of each set of readings were then combined into the grand mean. In taking this grand mean, as already explained, almost the entire weight was given to the last two sets of readings. The agreement between the different sets was best at the higher temperatures, 60° to 80°, and about equally good between 20° and 40° and 40° and 60°. All four sets of curves, while not agreeing very well as to the numerical value of the coefficient, do agree as to the general character of the results, which are, perhaps, not quite what would be expected. The unexpected feature is the change in the sign of the temperature derivative of the dilatation at the higher pressures. At the low pressures the dilatation is greater at the higher temperatures, but at the higher pressures the thermal dilatation becomes less at the higher temperatures. This essential feature is verified on all four sets of curves. There are indications that it may be an essential characteristic of the behavior of any normal liquid at high pressures, and that it is not peculiar to water alone. This is shown by the work on kerosene, and is also indicated by the work at present being done on still other liquids. This will be taken up in greater detail later. The other feature not to be expected is the increase in the value of the thermal expansion between 20° and 40° at the higher pressures. It is to be distinctly expected that the thermal dilatation will decrease with rise of pressure, as indeed it does for all the other intervals of temperature, but this rise between 20° and 40° is shown by all the sets of determinations and seems to be an undoubted fact. It is probably connected with some new abnormality in the behavior of water at the higher pressures, which may be connected in some way with the appearance of the new variety of ice.

The values finally taken as the best values for the thermal dilatation are the mean of the results of the four determinations, much the greater weight being given, as already explained, to the two latter determinations. Figure 2 gives these results, as also those of the other methods at the lower pressures. The agreement of the two best determinations at the higher pressures is about 5% for the lower temperature interval from 20° to 40°, 3% for the interval 40° to 60°, and 2% from 60° to 80°. The order of accuracy to be expected in these thermal measurements is not so great as that in the compressibility determinations, therefore, but perhaps the accuracy is as great as could be expected when one considers the smallness of the quantities involved, and the difficulty of making such measurements at high pressures. At any rate the absolute value of the coefficient cannot be very much in error. This is made probable by the agreement with the known values at atmospheric pressure. The accuracy is at least high enough to enable us to expect a fairly good quantitative description of the various thermodynamic quantities under high pressure, even those most sensitive to error. The calculation seems to be worth while carrying through in some detail, because such calculations seem never to have been undertaken for any substance, even for the low pressure range up to 3000 kgm., which is the range over which compressibility determinations have been previously made.

Discussion of Results.

The first necessity for a calculation of the various thermodynamic quantities is as accurate as possible a knowledge of the relation between pressure, temperature and volume over the entire pressure-temperature plane. It may be shown that this is sufficient to completely determine the thermodynamic behavior of the substance if in addition the behavior of the specific heat at constant pressure, for example, is known in its dependence on temperature at atmospheric pressure. This may be assumed to be known well enough for the present purpose. The first and the most important outcome of the present data is, therefore, the construction of a table giving pressure, volume, and temperature at sufficiently close intervals. In constructing this table the basis of computation was the compressibility as determined at 40°. This, together with the known value of the volume at 40° and atmospheric pressure, gave the volume as a function of the pressure down a line through the middle of the table at 40°. The values of the volume were tabulated for intervals of the pressure of 500 kgm., the values found graphically from smooth curves through the experimental points being so smoothed as to give smooth second differences. The values of the change of volume for intervals of 20° now were combined directly with these values to give the volume as a function of the pressure at 0°, 20°, 60°, and 80°. To find the intermediate values of the volume, smooth curves were drawn through these five points at every constant pressure, and the intermediate values so chosen as to given smooth values for the second differences over the entire temperature range. The values for the points below zero, which are also given in the table, were taken directly from the previous work, the values for the dilatation found there being kept without modification, but the present value for the compressibility at 0° being used. The differences so introduced may be seen by comparison of the two tables to be only slight.

The table gives the volume to only four significant figures, since this is as many as the variations in the values of the compressibility would entitle one to, but in making the calculations of the thermal expansion it was necessary to keep three significant figures for the expansion, which would mean five figures in the table.

The thermal dilatation per degree rise of temperature was determined from the values used in the construction of the table for the differences of volume at 5° intervals by dividing by 5, and using the result as the thermal expansion at the mean temperature. The values of the total change of volume for five degree intervals had been smoothed so as to give smooth second differences, so that the dilatation as found in this way was smooth also with respect to the second differences, and could be used directly to give the second temperature derivative of the volume at constant pressure.

The difference of thermal dilatation at different temperatures can evidently be combined with the known compressibility at 40° to give the compressibility as a function of the temperature.

These several quantities so determined; the compressibility, the thermal expansion, and the second temperature derivative of the volume, in their dependence on temperature and pressure, are the basis of most of the calculations of the quantities of thermodynamic interest to be given presently. The accuracy of most of these quantites is not so high but that they can be shown as well in figures as in tables, and this manner of presenting them has been chosen as giving the most ready general survey of the facts.

The tables and figures follow. The results are given simply for themselves, without much comment, except to call attention to the unexpected features, or those properties which seem to be peculiarly characteristic of high pressures. It would not be safe to generalize from the behavior of this one liquid, abnormal at low pressures, to the general behavior to be expected for any liquid for high pressures and the bearing on a possible theory of liquids. Such a general treatment must be reserved for another paper, when the data for more liquids are in hand.

TABLE IV.

Volume of Water as a Function of Pressure and Temperature.

Pressure. kgm./cm.	—20°,	—15°,	—10°,	—5°,	0°,	5°,	10°,	15°,	20°,	25°,	30°,	35°,	40°,	45°,	50°,	55°,	60°,	65°,	70°,	75°,	80°.
0			1.0017	1.0006	1.0000	0.9999	1.0001	1.0007	1.0016	1.0028	0.0041	1.0057	1.0076	1.0096	1.0118	1.0143	1.0168	1.0195	1.0224	1.0255	1.0287
500			.9795	.9778	.9771	.9778	.9786	.9796	.9808	.9821	.9837	.9854	.9873	.9894	.9916	.9940	.9965	.9992	1.0020	1.0049	1.0075
1000			.9598	.9584	.9578	.9589	.9602	.9616	.9630	.9646	.9663	.9681	.9700	.9721	.9743	.9766	.9791	.9816	.9842	.9869	.9896
1500		.9404	.9416	.9407	.9410	.9424	.9439	.9454	.9471	.9488	.9506	.9525	.9544	.9564	.9586	.9599	.9632	.9657	.9682	.9707	.9732
2000	.9228	.9235	.9243	.9252	.9260	.9276	.9293	.9310	.9327	.9345	.9364	.9383	.9403	.9423	.9445	.9467	.9489	.9513	.9537	.9561	.9585
2500	.9085	.9094	.9104	.9117	.9133	.9150	.9167	.9185	.9203	.9221	.9220	.9259	.9279	.9299	.9320	.9341	.9363	.9386	.9409	.9433	.9457
3000	.8963	.8972	.8984	.8997	.9015	.9032	.9050	.9068	.9087	.9106	.9105	.9144	.9164	.9184	.9205	.9226	.9247	.9269	.9292	.9314	.9337
3500		.8864	.8876	.8888	.8907	.8924	.8943	.8961	.8979	.8998	.8997	.9036	.9056	.9076	.9096	.9117	.9138	.9160	.9182	.9204	.9226
4000		.8766	.8774	.8786	.8807	.8825	.8843	.8861	.8880	.8889	.8897	.8936	.8956	.8976	.8996	.9016	.9037	.9058	.9080	.9101	.9123
4500			.8684	.8695	.8717	.8734	.8751	.8770	.8788	.8807	.8805	.8844	.8864	.8884	.8904	.8924	.8945	.8965	.8966	.9008	.9028
5000			.8599	.8610	.8632	.8649	.8666	.8684	.8702	.8721	.8719	.8758	.8778	.8798	.8818	.8838	.8858	.8879	.8899	.8920	.8940
5500				.8537	.8554	.8569	.8585	.8603	.8621	.8640	.8639	.8678	.8698	.8718	.8737	.8757	.8777	.8798	.8818	.8838	.8858
6000				.8464	.8480	.8494	.8509	.8527	.8545	.8564	.8654	.8603	.8623	.8643	.8662	.8682	.8702	.8722	.8742	.8762	.8781
6500					.8409	.8423	.8438	.8454	.8473	.8492	.8493	.8532	.8552	.8572	.8591	.8611	.8631	.8650	.8670	.8689	.8709
7000							.8370	.8386	.8404	.8424	.8425	.8465	.8485	.8505	.8524	.8544	.8564	.8583	.8602	.8621	.8640
7500							.8305	.8321	.8338	.8360	.8361	.8401	.8421	.8441	.8460	.8480	.8499	.8519	.8538	.8557	.8575
8000								.8259	.8275	.8298	.8300	.8340	.8360	.8380	.8399	.8419	.8438	.8457	.8477	.8495	.8513
8500								.8200	.8216	.8240	.8262	.8283	.8303	.8323	.8342	.8361	.8381	.8400	.8419	.8437	.8455
9000									.8160	.8185	.8208	.8229	.8249	.8269	.8288	.8308	.8327	.8346	.8364	.8383	.8401
9500										.8133	.8156	.8178	.8198	.8218	.8237	.8256	.8275	.8294	.8313	.8331	.8349
0000										.8083	.8107	.8129	.8149	.8169	.8188	.8207	.8226	.8245	.8264	.8282	.8300
10500											.8060	.8082	.8102	.8122	.8141	.8160	.8179	.8198	.8216	.8235	.8252
11000												.8036	.8056	.8076	.8095	.8114	.8133	.8152	.8170	.8188	.8206
11500												.7991	.8011	.8031	.8050	.8069	.8088	.8107	.8125	.8143	.8160
12000													.7966	.7986	.8005	.8024	.8043	.8062	.8080	.8098	.8115
12500													.7922	.7942	.7961	.7980	.7999	.8017	.8036	.8054	.8071

In presenting the results, the quantities have been arranged in order of simplicity of the thermodynamic formulae, which is also the order of directness with which they are derived from the experimental data.

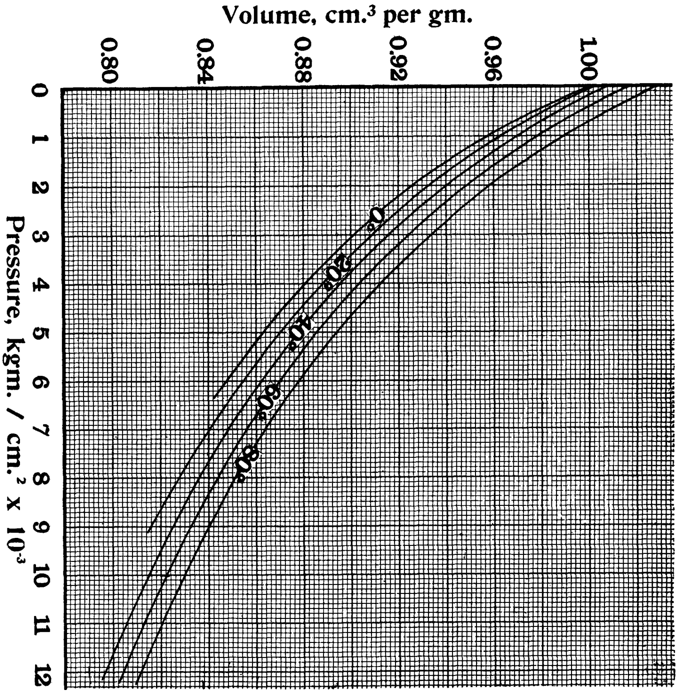

FIGURE 3. Isothermal lines for water, showing volume against pressure.

In Table IV are given the values of the volume for intervals of pressure of 500 kgm., and intervals of temperature of 5°. The table does not require comment. It was computed in the way already described. The values of the volume at intervals of temperature of 20° are shown as a function of the pressure in Fig. 3. The figure does not show the results as accurately as the table, but enables one to form a clearer mental picture of the nature of the results. The curves, on the scale of the figure, do not show any abnormalities to the eye, except in the neighborhood of the origin, where the well known negative expansion at 0° results in the curves drawing together.

There are various abnormalities besides those in the neighborhood of 0°, however, as will be shown by the other figures.

With regard to the compressibility there seems to be some variance of usage, so that it will be well to call attention to the fact that the quantity used throughout this paper in the sense of compressibility is

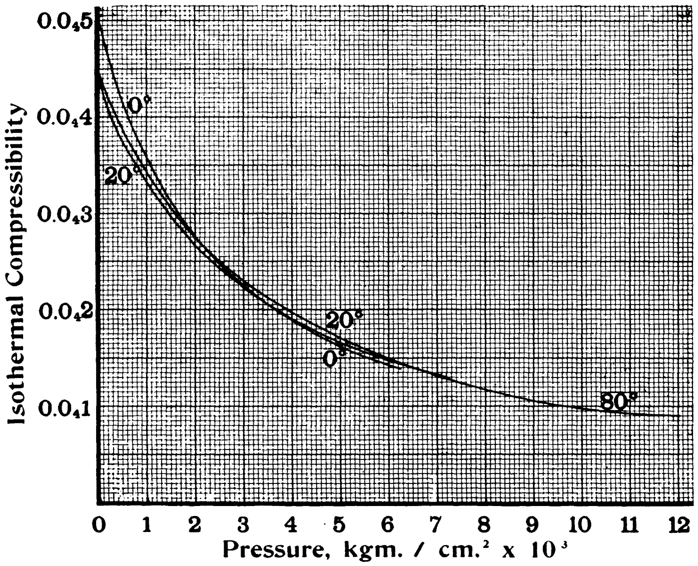

FIGURE 4 The isothermal compressibility of water, $\left(\frac{\partial v}{\partial p}\right)_t$ against pressure.

the derivative $\left(\frac{\partial v}{\partial p}\right)_t$. Sometimes the expression $\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_t$ is used in the same sense. Figure 4 shows the compressibility, that is, the analytic expression $\left(\frac{\partial v}{\partial p}\right)_t$, as a function of the pressure at 0°, 20°, and 80°. It would have made the figure too crowded to have tried to show the values for 40° and 60° also. The complete values for the five standard temperatures are shown in Table V separately, however. The figure shows the well known abnormality in the compressibility at the low pressures, namely a higher compressibility at the lower than at the higher temperatures. This abnormality disappears above 50°, and from here on the compressibility increases with rising temperature. The figure shows that at 80° the initial compressibility is higher than at 20°, although it has not yet risen to the value at 0°. In addition to the abnormality at low pressures, the curve shows also a slight

TABLE V.

Compressibility of H_2O.

Pressure, kgm./cm.^{2}	$\left(\frac{\partial v}{\partial p}\right)_t$, cm.^{3}/gm.				
	0°.	20°.	40°.	60°.	80°.
	.0000	.0000	.0000	.0000	.0000
0	504	453	440	438	450
500	417	381	371	373	388
1000	360	336	328	332	346
1500	313	298	292	296	306
2000	276	267	263	267	274
3000	225	223	222	224	229
4000	189	191	191	193	198
5000	162	166	165	166	170
6000	143	148	146	147	149
7000		133	130	130	132
8000		121	117	117	119
9000			104	104	105
10000			096	096	097
11000			091	091	092
12000			089	089	090

abnormality at the higher pressures in the neighborhood of 6500 kgm. Here the compressibility at 20° rises and at the melting point of ice VI, it has become higher than the compressibility at 80°. The thermal dilatation shows abnormality in the same locality; it would seem to be connected in some way with the appearance of the new variety of ice, but the exact connection cannot at present be stated.

The large change in the value of the compressibility brought about by pressure should be noticed, amounting at 12,000 kgm. to a decrease of five fold. Furthermore the rapid flattening of the curve at the higher pressures also should be commented on. The curve gives the appearance, for the pressure ranges used here, of becoming asymptotic to some value greater than zero. Of course this cannot really be the case for infinite pressures, for otherwise we should have the volume completely disappearing for some finite value of the pressure, but it may indicate the entrance of another effect at the higher pressures, which may persist in comparative constancy for a greater range of pressure than will ever be open to direct experiment, such an effect as the compressibility of the atom, for example. This possibility has been already mentioned and made plausible from the data of the preceding paper.

If instead of the compressibility as defined above, the quantity $\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_t$, which in this paper will be called the relative compressibility, is plotted, a curve of the same general character as that shown will be obtained.

The compressibility may also be plotted against a different argument than the pressure. For many purposes the pressure is perhaps not the most significant independent variable that might be chosen. This is because the external pressure is not a measure of what is happening inside of the liquid. We conceive a liquid as composed of molecules in a state of constant motion and of collision with each other, acted on also by attractive forces between each other. The effect of these attractive forces is to produce at the interior points a pressure which may be much higher than the external pressure. The external pressure is equal to the interior pressure diminished by the amount of the attractive pressure drawing the molecules to the interior at the exterior surface, where the attraction is an unbalanced action in one direction. The amount of the unbalanced pressure at the outside depends in a complicated way on the law of attraction between the molecules, on their mean distance apart in this surface layer, and on the distribution of velocities in this layer. The external pressure required to hold the liquid in equilibrium is, therefore, largely a surface phenomonon, and is connected in a complicated way with the state of affairs at inside points. A more significant independent variable, therefore, would be one involving only the condition of the molecules on the average throughout the mass, and not one dependent on the surface layer. There are only a few such quantities depending on the state of the liquid at interior points. Any quantities involving in any way the constancy of pressure or of entropy, for example, do depend on the complicated action of the surface layer. One of the quantities which is independent of this surface layer, however, is the volume. In many theoretical considerations the use of the volume as an independent variable is known to produce simplifications.

If the volume, instead of the pressure is taken as the independent variable for the compressibility, curves are obtained of the same general appearance as when the pressure is used for the variable. The compressibility falls with decreasing volume, and the curvature is in the same direction as when the pressure is the independent variable. The same general characteristics are also shown if the relative compressibility instead of the compressibility is plotted against the volume. The two sets of curves, for the compressibility and the relative compressibility, do show one feature in common, however, different from the curves when the pressure is used as the variable. This is the fact that the compressibility is always lower for the same volume at the higher temperature. This is true throughout the entire range of volume used; there is no crossing of the curves indicating abnormalities, such as is the case when the pressure is used as the variable. This is what one would expect on the kinetic theory. A liquid, at two different temperatures but at invariable volume, differs only in the violence of the motion of its molecules. At the higher temperature, the kinetic pressure due to the motion is greater, and so the resistance offered to change of volume under a given increase of external pressure is greater when the temperature is higher.

Fig. 5 shows the thermal dilatation as a function of pressure at various temperatures. The thermal dilatation plotted in the figure is the expression $\left(\frac{\partial v}{\partial t}\right)_p$ instead of the expression $\frac{1}{v}\left(\frac{\partial v}{\partial t}\right)_p$, which is sometimes used as the dilatation. The usage adopted here for the dilatation is analagous to that explained above for the compressibility. The values listed in the figure were obtained from the table of volumes in the manner already described. The curve at 0° was obtained from the data of the previous paper for the low temperatures, but in that paper the mean value of the thermal expansion for the range 0°–20° was given, whereas here the instantaneous value at 0° is given instead. The substitution of the instantaneous for the mean dilatation produces no change in the general character of the curves, however.

The points at the higher temperatures were obtained from the data of this paper alone. There are two striking features that call for special comment. The first of these is the abnormal behavior of the curve for 20°. In the initial stages, the dilatation rises with increasing pressure, unlike normal liquids, but this merely indicates the return of water to the normal behavior to be expected at high pressures. At about 3500 kgm. the curve at 20° has reached a maximum and begins to descend with increasing pressure, as it does for the curve at 0°. But the descent continues for only a little way, and at 5500 kgm. the curve begins to rise again, indicating the entrance of a new abnormality. The abnormality is not so striking or so great in amount as that in the neighborhood of 0° and atmospheric pressure. The abnormality at 20° continues for about 2500 kgm., up to 8000, where the curve is terminated by the entrance of the solid phase, but the direction of the curve has already begun to change, indicating that if it could be continued, this abnormality also would probably disappear at higher pressures. As to the question of experimental error here, there would seem to be no room for doubt as to the actual existence of this new abnormality, for it was shown by all four of the dilatation curves, even those taken before the method was got to running satis-

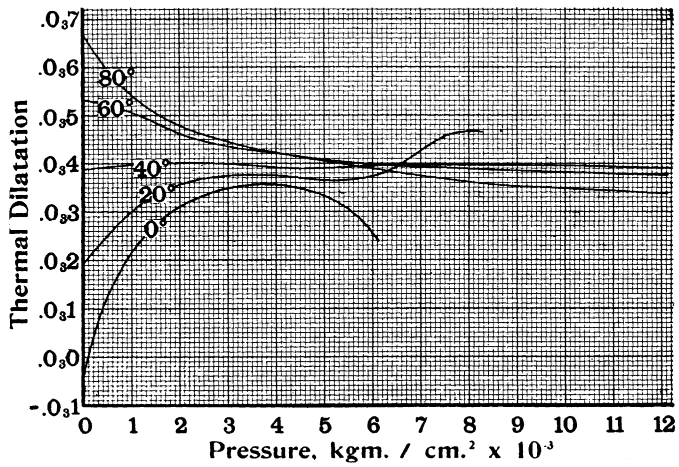

FIGURE 5. The dilatation of water, $\left(\frac{\partial v}{\partial t}\right)_p$, against pressure.

factorily, and in which the accuracy was not very high. The curves at the higher temperatures behave as one would be prepared to expect in the region of low pressures. The curve for 40° shows vestiges of the abnormal behavior at the low pressures, namely slight initial rise of dilatation with rising pressure, followed by a fall, but the curves at the higher temperatures, 60° and 80°, show the regular initial decrease with rising pressure shown by all normal liquids. But at higher pressures, the behavior of all three of these curves, for 40°, 60° and 80° is different from what might be expected. The unexpected feature consists in the crossing of the curves, all in the vicinity of the same pressure, 5500 kgm., so that at higher pressures the thermal dilatation at the higher temperatures is lower than it is at the lower temperatures. It has been already remarked that there are indications, both from the present work and from that of Amagat, that this may be the behavior for any normal liquid at sufficiently high pressures. The comparative constancy of the thermal dilatation at the higher pressures, is also a matter perhaps not to be expected. Thus the expansion at 40° remains nearly constant over the entire range of pressure, while the compressibility has in the same range dropped from 44 to 9. It was distinctly expected, before these measurements were taken, that the dilatation would show the greater variation with pressure, so that the effect of temperature on the volume would tend to disappear at the higher pressures, but such is not the case.

The relative thermal dilatation may be plotted against pressure, as was the relative compressibility. The curve shows no striking features. The curve plotting relative dilatation against volume has also been plotted, and this is the same in general character as the others. The slight differences consist in an accentuation of the abnormalities in the neighborhood of 5500 kgm., and the fact that at the lower volumes, that is at the higher pressures, the dilatation against volume increases with decreasing volume for 40° and 60°, but decreases for 80°.

These figures for the thermal dilatation and the compressibility complete those which are obtainable directly from the table. Other quantities of thermodynamic interest may be obtained by combining these, however. Perhaps the simplest of these quantities are those connected with the absorption of energy when the pressure is changed at constant temperature. The first of these is the actual mechanical work done by the external pressure in compressing the liquid at constant temperature. This of course is simply the expression

$W = \int p \left(\frac{\partial v}{\partial p}\right)_t dp.$ It was obtained by a mechanical integration from curves similar to the volume curves of Figure 3, drawn on a larger scale. For this purpose the integrating machine owned by the mathematical Department of Harvard University was used. The actual value of the mechanical work at any pressure is of course dependent on the temperature, but since the variation is so slight that it would have been impossible to show it in the figure (see Figure 6), the work of compression is plotted for only the one temperature, 60°. Although the change of external work with temperature was too slight to show in the diagram, the change with temperature was nevertheless taken account of in making the calculations of the quantities depending on it to be described immediately. After the first 4000 kgm. it is seen that the curve becomes very approximately linear. The curve for a substance which retains the same compressibility unchanged over a wide pressure range, as steel for example, is a parabola, the work increasing directly as the square of the pressure. That this curve for water becomes linear, means that the compressibility decreases so fast with increasing pressure that the decrease in the yield

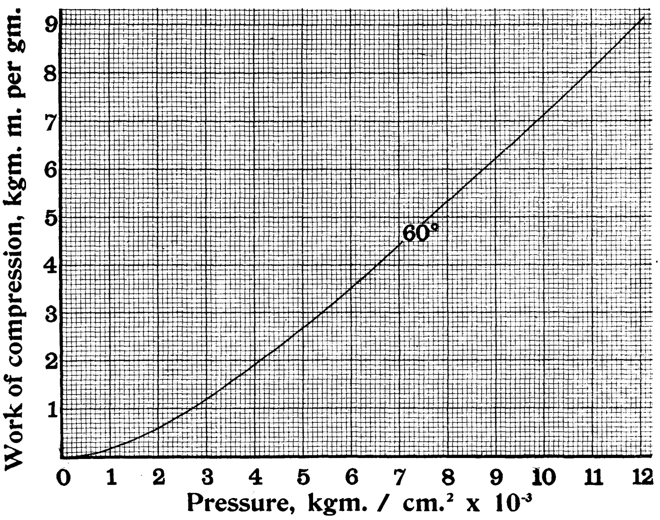

FIGURE 6. The mechanical work of compression at 60°.

of the liquid for a given increment of pressure decreases almost at the same rate that the pressure itself increases.

The total heat given out during an isothermal compression may be derived from the formula $\left(\frac{\partial Q}{\partial p}\right)_\tau = -\tau\left(\frac{\partial v}{\partial \tau}\right)_p$. This quantity is shown in Figure 7. The figure does not call for especial comment. The rapid change in the direction of the isothermal lines in the vicinity of the origin due to the abnormal behavior at low temperatures and pressures is manifest from the figure, as also the slight abnormalities at the upper ends of the 0° and the 20° curves, already commented upon in other connections. Beyond 5000 kgm. the curves for all temperatures tend to become linear and parallel to each other.

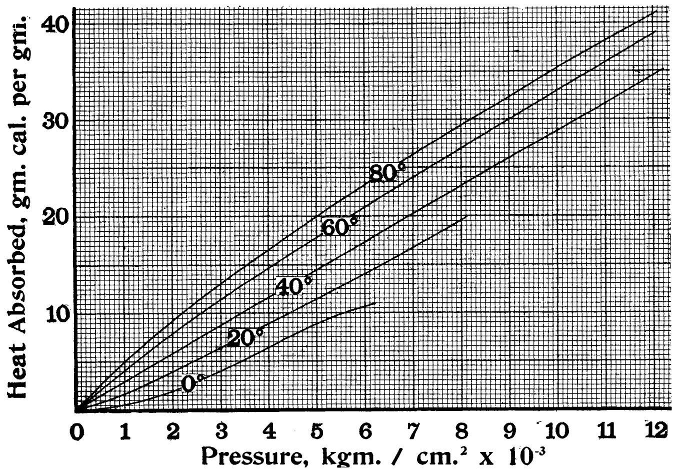

FIGURE 7. The heat given out by water during an isothermal compression.

These two quantities, the heat liberated in compression and the mechanical work, combine to give the change of internal energy along an isothermal, this change of energy being equal to the difference of the heat and the mechanical work. The change of energy so calculated is shown in Figure 8. The change is a decrease, which continues at all temperatures up to the highest pressures. In the previous paper a value of this quantity was given, confessedly inaccurate, since in the computation the mean thermal dilatation between 0° and 20° had been used instead of the actual dilatation at 0° or 20°. The curve so obtained had the characteristics of the curve now given for 0°, but the maximum at the top was much more strongly accentuated than in the present figure. It was surmised in the previous paper that at high enough pressures the internal energy of all liquids would probably increase instead of decrease along an isothermal. This surmise seemed plausible because one would expect that at high enough pressures the energy stored up as strain in the interior of the molecules in virtue of the extremely high pressures would more than counterbalance the work done by the attractive forces of the molecules themselves as they were brought closer together by the action of the pressure. This present figure shows that this is not the case, however, for the range of pressure reached here. The lower temperature, 0°, is the only one at which this reversal of the direction of the change of internal energy manifests itself, and this change, in comparison with the other curves, is now seen probably to be an effect of the other abnormalities shown at low pressures and temperatures. Nevertheless it would still seem as if at very high pressures the energy must increase instead of decrease along an isothermal, but the only indication of it from the present curves is in the direction of curvature, which is in the direction

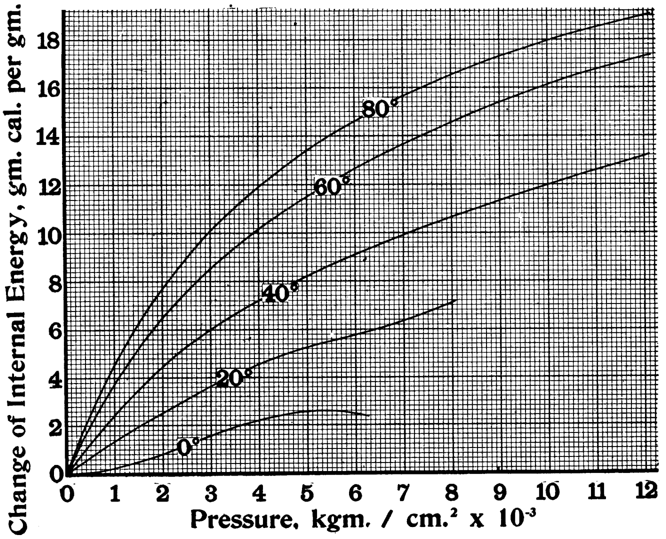

FIGURE 8. The decrease of internal energy of water during an isothermal compression.

to indicate the possibility of a maximum and a reversal of direction at higher pressures. The pressure for a maximum, however, if there is one, is much beyond the reach of any at present attainable. Within the pressure range of these measurements, the attraction between the molecules still remains the dominant feature, so that the work done by the attractive forces and liberated as heat much more than suffices to overbalance the mechanical work of compression.

The internal energy of a substance is one of those quantities which depend only on the properties of the mass of the substance at interior points and do not involve the action of the surface layer. Change of energy plotted against volume shows in the first place that the change of internal energy is much more nearly a linear function of the volume than it is of the pressure. The average slope of the isothermal lines of energy increases rapidly with rising temperature for the lower temperatures, but the two curves for 60° and 80° run nearly parallel to each other for their length. Abnormalities are shown at the upper ends of the 0°, 20° and the 40° curves, and the 0° curve shows the same maximum as it does when plotted against pressure. The origin, of course, for the curves at different temperatures does not coincide as it does for the same quantities when plotted against pressure.

One other quantity may be simply determined in terms of the compressibility and the thermal dilatation alone, the so-called pressure coefficient, that is, the change of pressure following a rise of temperature when the temperature is raised by 1° at constant volume. This quantity is given immediately in terms of the compressibility and the thermal dilatation by the well known formula,

$$\left(\frac{\partial p}{\partial \tau}\right)_v = -\left(\frac{\partial v}{\partial \tau}\right)_p \Big/ \left(\frac{\partial v}{\partial p}\right)_\tau .$$

It is shown plotted in Figure 9. The curves for 0° and 20° show anomalies, as is indicated by the unexpected direction of curvature. The other curves for the higher temperatures seem to be regular enough, though of course it cannot be told whether the course of these curves is the same as that which would be shown by a normal liquid or not. At the upper ends of the high temperature curves, the curvature is in such a direction that if they were continued far enough the pressure coefficient would decrease instead of increasing with rising pressure.

This quantity, the pressure coefficient, has been made the basis of theoretical speculation. It has been enunciated as a law, approximately true, by Ramsay and Shields, that the pressure coefficient is a function of the volume only. This means that if the coefficient were plotted against volume instead of pressure the curves for all five temperatures would fall together. That this is not the case for water at high pressures is shown very distinctly in Figure 10. At the lower pressures and the larger volumes, the curves for the different temperatures are very widely separated. The abnormality on the curve at 0° in the neighborhood of the locality where the new variety of ice makes its appearance is very striking. At the higher pressures the curves do draw together, but they are not approaching coincidence, for they cross in the neighborhood of a volume of about 0.85. It does not seem likely that the entire failure of coincidence throughout the whole range of pressure can be due to abnormalities, since even at low pressures water is nearly normal at the higher temperatures, and certainly at the higher pressures and temperatures we have every reason to expect that its behavior is quite like that of other liquids.

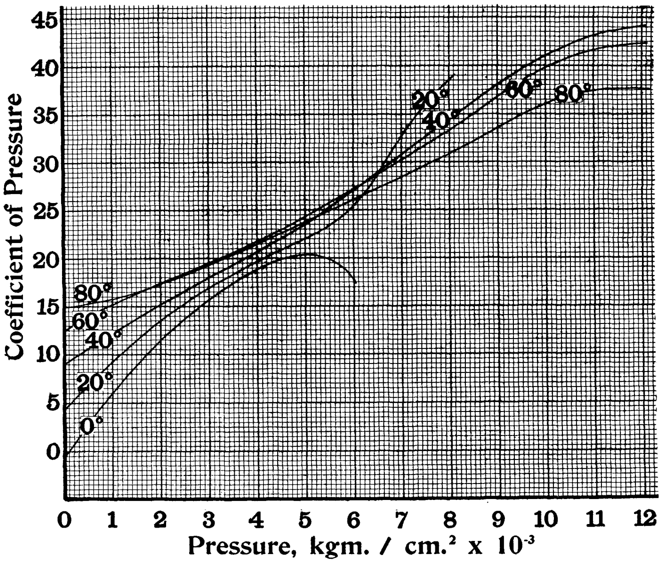

FIGURE 9. The pressure coefficient, that is the change of pressure accompanying a rise of temperature of one degree, as a function of the pressure.

This completes the list of quantities which can be deduced directly from the compressibility and the thermal dilatation. Other quantities of thermodynamic interest involve the specific heats, and these in turn involve the second temperature derivative of the volume.

The first of these quantities is the specific heat at constant pressure. This is given by the thermodynamic equation $\left(\frac{\partial C_p}{\partial p}\right)_\tau = -\tau\left(\frac{\partial^2 v}{\partial t^2}\right)_p$. It will be seen that only the derivative of the specific heat is given by the data as directly determined. In order to obtain the specific heat itself, the derivative, obtained from the tables in a manner already described, must be integrated. This integration was performed mechanically, in the same manner as the integration for the mechanical work of compression. The results are shown in Figure 11. The values for the specific heat as a function of temperature at atmospheric pressure were taken from the steam tables of Marks and Davis.[8] These values seem to be open to some slight question at the present time due to experimental work done by Bousfield [9] since the publication of the tables, but in any event the possible error is slight, too slight to be visible on the scale of the figure. The curves show the now expected abnormalities at 0° and 20°. The striking feature about the curves for the higher temperatures is the very rapid increase of the specific heat with rising temperature at the higher pressures. The specific heat at first decreases on all the curves except at 0°, but passes through a minimum, and then increases. The pressure of the minimum rapidly becomes less with rising temperature, and is situated at 6500 kgm. for 40°, 5500 kgm. for 60°, and at 1100 kgm. for 80°. At 80° the specific heat rises rapidly beyond the minimum, reaching the value 1.17 at 12000 kgm.

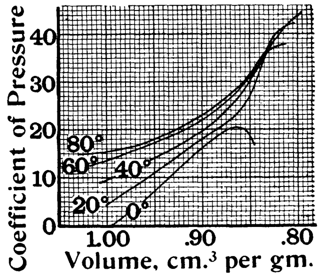

FIGURE 10. The pressure coefficient of water as a function of the volume.

Any valid characteristic equation should predict the behavior of the specific heat at high pressures as well as giving the volume in terms of pressure and temperature, since from the equation the second temperature derivative of the volume may be found. The equation of Tumlirz [10] has been mentioned in the preceding paper as giving perhaps as good agreement as any with the previously known facts over a pressure range of 3000 kgm. This equation would predict a continuous diminution in the specific heat up to infinite pressures, the limiting value being very approximately 0.5. It was shown in the preceding paper that there is some new effect introduced at the high pressures which does not make itself felt at the low pressures, with the result that an extrapolation to infinite pressures from the behavior for the first 3000 kgm. is not safe. This was shown in that paper by the behavior of the volume, which tended to decrease more rapidly at the high pressures than was predicted by the formula. The present data also show that there is a new effect at the high pressures, and indicate that the effect, whatever it is, is such as to have a much greater influence on the specific heats than on the volume itself.

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[8] Marks and Davis, Steam Tables. (Longmans, Green, and Co.)

[9] W. R. and W. E. Bousfield, Trans. Roy. Soc. (A), **211**, 199–251 (1911).

[10] Tumlirz, Sitzber. Wien, Bd. **68,** Abt. IIa (Feb., 1909), pp. 39.

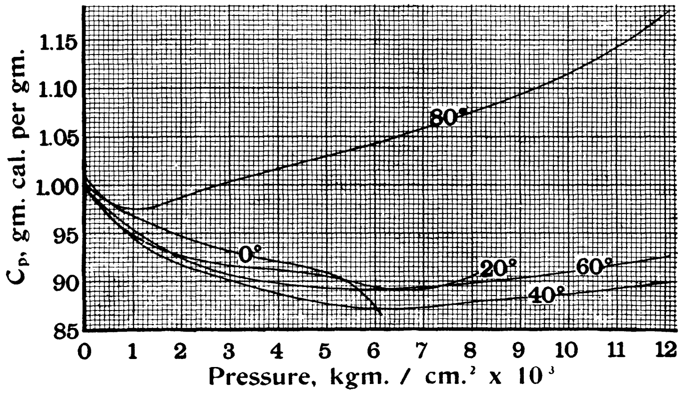

FIGURE 11. The specific heat at constant pressure of water as a function of the pressure.

The specific heat at constant volume may be found from the specific heat at constant pressure by means of the formula, $C_p - C_v = -\tau \frac{\left(\frac{\partial v}{\partial \tau}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_\tau}$. This quantity, so calculated, is shown in Figure 12. The same abnormalities are shown at 0° and 20° as were shown in the curves for C_p. The curves for 40° and 60° decrease for nearly their entire lengths, although they are just beginning to rise at the very highest pressures, but the curve for 80° shows the same sharp turning point and the same rise through the greater part of its length as the curve for C_p. This quantity, the specific heat at constant volume, has more theoretical significance than the other specific heat, since this represents the heat going into the rise of internal energy of the liquid when the temperature rises, and does not involve the work done against external pressure in expanding the liquid. The external work involves in a complicated and at present unknown way the action of the surface layer, while the specific heat at constant volume does not contain this surface effect. This specific heat is therefore one of the quantities mentioned in the beginning as having significance because it does not involve the unknown attractive forces between the molecules as displayed in the surface layer. In order to show this independence of the surface layer, of course C_v should be plotted against a variable not itself involving the action of the layer. It is evidently not adequate, therefore, to plot C_v against the pressure as as been done in Figure 12. C_v plotted against volume may be expected to show this independence of the action of the surface layer. It is shown so plotted in Figure 13. The figure is of the same general character as that in which it is plotted against pressure, but the separation of the curves for the different temperatures is greater, partly because the curves do not start from a common origin. The minimum on the curves for 40° and 60° comes at a lower pressure than it does in the former figure, and the upper end of the 80° curve is perhaps a trifle steeper at the upper end, but there are no essential differences. The entire behavior of the curves is not what one would

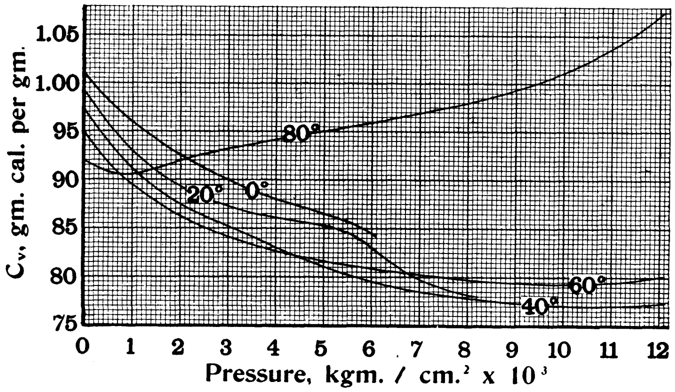

FIGURE 12. The specific heat at constant volume of water as a function of the pressure.

expect from the ordinary theoretical considerations, however. It is usually considered that when the volume of a substance is kept invariable all, or else a fixed fraction, of the heat put in during a rise of temperature goes toward increasing the kinetic energy of the molecules. This is because the temperature is supposed to be proportional to the energy of translation of the molecules, and therefore, because of the law of the equipartition of energy, to the total energy of the molecules. We should expect, therefore, that the input of energy required to raise the temperature by a specified amount would involve only the interval of temperature, and would be independent of the absolute value of the temperature and of the volume. The curves show most convincingly that this is not the case. This suggests that in formulating a theory of liquids it would be well to scrutinize pretty carefully several assumptions that underlie the above considerations, namely that the temperature is proportional to the kinetic energy, that a fixed fraction of the total energy of the molecules is kinetic, and that the law of the distribution of velocities is independent of temperature.

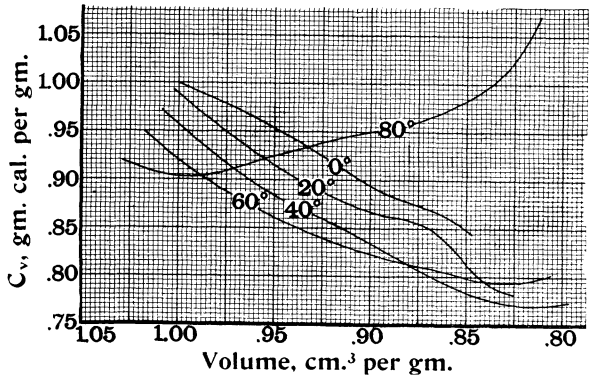

FIGURE 13. The specific heat at constant volume of water as a function of the volume.

Another quantity of thermodynamic interest which may be found in terms of the specific heats is the thermal effect of compression, that is the rise of temperature in degrees accompanying a change of pressure adiabatically of one kgm. per sq. cm. This may be computed by the thermodynamic formula $\left(\frac{\partial \tau}{\partial p}\right)_\varphi = \frac{\tau\left(\frac{\partial v}{\partial \tau}\right)_p}{C_p}$. The results so calculated are shown in Figure 14 for the five standard temperature intervals. The character of the curves is the same as that shown so many times before, namely a rise to a maximum and then a fall at 0°, the abnormal behavior at the upper end of the 20° curve, and the more or less regular behavior of the three curves for the higher temperatures, with the crossing of the high temperature curves below the low temperature curves at the higher pressures. In the preceding paper only the approximate values for the very lowest temperature interval could be found. The calculation was based on the mean value of the dilatation between 0° and 20°. The general character of the curve was the same as that found here for 0°, namely a rise to a maximum and then a fall.

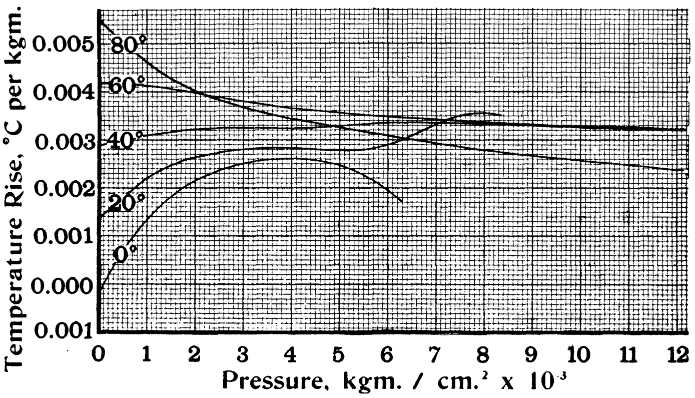

FIGURE 14. The adiabatic rise of temperature of water against pressure.

Finally it is possible to compute from the quantities in hand the difference between the isothermal and the adiabatic compressibilities. This is found from the formula $\left(\frac{\partial v}{\partial p}\right)_\varphi - \left(\frac{\partial v}{\partial p}\right)_\tau = \frac{\tau}{C_p}\left(\frac{\partial v}{\partial \tau}\right)_p^2$. The results are shown in Figure 15. The general character of the results is exactly the same as those previously given for the temperature effect of compression. Here again, the results at the lowest temperature agree with those of the previous paper which were based on a mean value for the dilatation.

PROPERTIES OF KEROSENE UNDER PRESSURE.

In the course of the experiment other data were gathered incidentally which are of interest for themselves, and which will now be given. First of these is the compressibility and the thermal dilatation of kerosene. It was not necessary to determine this quantity in order to find the corrections to be made for the distortion of the vessel, but since half the work was already done in determining the effect with the cylinder partly filled with kerosene and the other part filled with bessemer steel, it seemed worth while to make the additional run necessary to determine the pressure and temperature effects on the kerosene. Not so many determinations were made of these quantities for kerosene as were made for the water. The results are given in Table VI. The curves showing the total thermal change of volume for 20° intervals are shown in Figure 16. This figure is the analog of Figure 2 for water. The results are very different. At the lower pressures the dilatation is greater at the higher temperatures, as it is for all normal substances, but with rising pressure the effect is reversed, the dilatation becoming greater for the lower temperatures. This is the same behavior which takes place for water at higher temperatures after it has regained normality. But above 5000 kgm. the kerosene shows other abnormalities quite different in their charac-

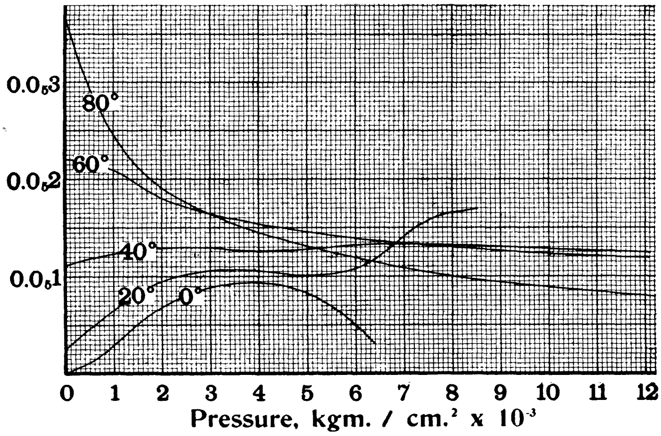

FIGURE 15. The difference between the adiabatic and the isothermal compressibilities of water.

ter from those of water. This is shown plainly in the figure as a separation and then a drawing together again of the curves. The curve for 20°–40° between 6000 and 8000 and the curve for 60°–80° beyond 9000 accomplish this separation and drawing together again

TABLE VI.

Volume of Kerosene as a Function of Temperature and Pressure.
(The volume at 0° and atmos. pressure is taken as unity.)

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$	Volume.			
	20°.	40°.	60°.	80°.
0	1.0221	1.0412	1.0611	1.0819
1000	.9643	.9763	.9885	1.0010
2000	.9274	.9376	.9468	.9553
3000	.8995	.9086	.9165	.9239
4000	.8781	.8861	.8931	.8997
5000	.8606	.8681	.8747	.8807
6000	.8456	.8529	.8592	.8647
7000	.8323	.8396	.8456	.8508
8000	.8201	.8275	.8334	.8384
9000	.8090	.8161	.8220	.8269
10000	.7989	.8057	.8115	.8164
11000	.7897	.7960	.8017	.8069
12000	.7815	.7872	.7928	.7982

by rising with rising pressure, exactly as do some of the curves for water. The abnormality is doubtless due to an entirely different cause, however. In this case the effect is to be explained by the delayed freezing of the kerosene. Kerosene is not a simple pure substance, but is a mixture of several components with different melting points. Freezing under these conditions is not sharp, but is spread out over a considerable interval of temperature or pressure as the case may be. Neither is there any necessity that the freezing should ever be perfectly complete, as indeed it is probably not. This may be shown at atmospheric pressure by plunging the kerosene into solid CO_2. The effect is to change the kerosene to a white pasty mass, like white vaseline. The pressure at which this transition occurs will rise with increasing pressure. The existence of a transition point, if there were one perfectly sharp, would be shown by an abrupt rise of the curve by an amount corresponding to the change of volume on freezing. But with the delayed freezing which takes place here due to the separation out of the separate components from a solution of varying strength, this abrupt rise becomes converted into a gradual rise extending over a fairly wide pressure range. Furthermore, the mean pressure at which this rise takes place increases with rising pressure, just as the ordinary freezing point is raised by increasing pressure. These features are all clearly shown in the diagram. At the extreme right of the diagram, at pressures over 12,000 kgm., there is evident the beginning of the reversal of the effect,

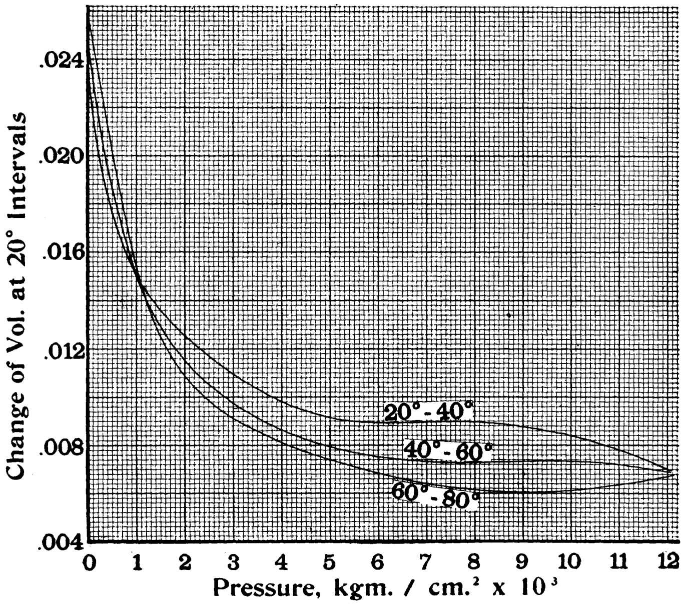

Figure 16. The change of volume of kerosene at constant pressure for a rise of temperature of 20°.

that is, the curves are going to cross again, and the thermal dilation become greater at the higher temperatures. This may possibly indicate a reversal of the reversal of the effect mentioned above for liquids, but more probably the meaning is simply that at pressure above 12,000 the substance is practically a solid, and that for solids the reversal of the effect found in liquids at high pressures does not occur.

There is one bearing which these observations have on the previous data which should perhaps be mentioned. This is in connection with the delayed freezing. Whenever freezing takes place there is usually the possibility of subcooling before separation to the solid form takes place. The amount of subcooling usually taking place depends on the nature of the liquid. In some it is very considerable, while in others it is negligible. If such subcooling took place here, it would produce irregular results, because the change of volume in the kerosene transmitting pressure to the water would not always be the same under the same pressure. The only answer to be made to this objection is that in this experiment the subcooling was not great enough to produce sensible irregularity. No discrepancies were found in the data suggesting that they were due to this effect. It was feared in the beginning of the work that the effect might be very troublesome, but such did not turn out to be the case.

Also with respect to the solidification of the kerosene, the experiments showed that the solidification could not be complete, but the kerosene, even at the highest pressures, must remain a pasty mass like vaseline in nature, always capable of transmitting pressure nearly hydrostatically. But that on the other hand the kerosene does undoubtedly become pretty stiff under pressure has been already shown in the course of some measurements on the linear compressibility of steel rods.

The second bit of data collected incidentally in the course of the work was a measurement of the expansion and the thermal dilatation of the high temperature variety of ice.

The Compressibility and Thermal Dilatation of Ice VI.

Although these data are not directly concerned with the properties of liquid water, which forms the subject matter of this paper, still it was so easy to obtain them without any modification in the arrangement of the apparatus, that it was thought worth while to measure them. In the previous paper on the properties of water and the several varieties of ice, a very rough experimental value for the compressibility was given, as also a computation of the approximate compressibility, neglecting the thermal dilatation of the ice, for which no experimental value was found at that time. These measurements here include a direct measurement of the thermal dilatation, and two different determinations of the compressibility by two different methods. The value for the dilatation may be combined with the already determined values for the volume of the liquid and the change of volume when ice VI separates out, to give a third independent value for the compressibility.

The determinations of the dilatation will first be described. This was found in the same manner as the dilatation of the liquid, by changing the temperature at constant mean pressure, and measuring the change of pressure brought about thereby. Three determinations of this were made for the combination of ice and kerosene, and two for the combination of kerosene and bessemer. The agreement of the different determinations was within 2% of the mean. The dilatation was found between 0° and 20° at a mean pressure of 10,000 kgm. The correction introduced by the thermal dilatation of the bessemer cylinder in the control experiment is fairly large here, being about 25% of the entire effect. The value assumed for the cubic dilatation was 0.000036, which is the value for atmospheric pressure. The effect of pressure is to decrease this number slightly, which would result in a larger value for dilatation of the ice. The effect of pressure on this quantity is, however, very small, and the error so introduced is probably negligible. The mean dilatation found in this way for the 20° above 0° at 10,000 kgm. was 0.00241 $cm.^3/gm.$, or 0.000120 $cm.^3/gm.$ per degree. This is considerably less than the dilatation of the liquid in this neighborhood, for which the value 0.00040 has been found previously.

This value for the dilatation may now be combined with the other data for the liquid and the solid to give the compressibility of the solid along the equilibrium curve. For this we have the following data: vol. of 1 gm. of water at 0° and 6360 kgm., 0.8428 $cm.^3$, and at 20° and 9000 kgm. (these are the equilibrium pressures at these temperatures) 0.8160 $cm.^3$. For the change of volume when the liquid freezes to the solid we have at 0°, 0.0916, and at 20°, 0.0751. This gives for the volume of ice at the equilibrium pressures at 0° and 20° the values 0.7512 and 0.7409 respectively. The decrease of volume of the ice along the equilibrium curve is 0.0103. Part of this is an increase due to rise of temperature, which according to the above data is 0.0024. This leaves a decrease of 0.0127 to be accounted for by the increase of pressure of 2640 kgm. which gives a mean compressibility over this range of 0.0000048, a little more than one third of the compressibility of the liquid over the same range.

The direct determination of the compressibility of the ice was made by two different methods. One of these was the same as that used roughly in the preceding paper, that is by finding the difference of the slope of the curves plotting piston displacement against pressure above and below the transition point to the solid. The values obtained in the preceding paper for this were very rough. In these determinations the cylinder was very much more carefully seasoned, and the readings were made with all the precautions which had been suggested by all the experience of this paper. Two determinations of this quantity were made at 0° and also two determinations at 20°. The two values for the difference of compressibility differed by 2.5% at 0° and by 0.7% at 20°. The value found for the difference was 0.0000087 at 0° and 0.0000067 at 20°. Combining with the values given already for the compressibility of the liquid, this gives for the compressibility of ice VI 0.0_549 at 0° and 6360 kgm., and 0.0_543 at 20° and 9000 kgm. Mean 0.0_546.

The second method for determining the compressibility was exactly the same as that for finding the same quantity for the liquid, comparing the displacements when the apparatus was filled with ice and kerosene with those when the ice was replaced by bessemer steel. This determination was made over a wider pressure range, to find if possible the variation of compressibility with pressure. No variation with pressure could be found over a range of 4500 kgm. at 0° and 3300 kgm. at 20°. The absolute values do not agree with those found by the two other methods, however, the figures being 0.0_531 at 0° and 0.0_535 at 20°. The cause of the discrepancy is not clear, but is probably connected in some way with the hysteresis of the cylinder. The hysteresis was not regular for these small pressure ranges, being at times almost negligible, and again being as large as for almost the entire pressure range from atmospheric pressure to the maximum. There seems little question but that the greater weight is to be attached to the values found by the first two methods. This third determination does show, however, that the variation of the compressibility with pressure and temperature over this range is so small as to be beyond the accuracy of these measurements. In selecting the best probable value for the compressibility the only weight that will be assigned to this third determination is in slightly lowering the mean of the other two.

The final most probable values for Ice VI are as follows: for the compressibility 0.0_545, and for the thermal dilatation 0.000120 cm.^{3}/ gm. over the range 6360–10,000 kgm. and 0° to 20°.

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